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INVESTIGATIONS OF THE KINETICS AND EFFECTS OF DEGRADATION OF PAPER-BASED MATERIALS

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CHAPTER 4

LIST OF ACRONYMS

AKD	alkyl ketene dimer
ANOVA	analysis of variance
ASA	alkenyl succinic anhydride
ATR	attenuated total reflectance
CED	cupriethylenediamine solution
CEPI	confederation of european paper industries
DMAc	LiCl/n,n-dimethylacetamide
ECF	elemental chlorine free
FTIR	Fourier transform infrared spectroscopy
FWA	fluorescent whitening agent
GCC	ground calcium carbonate
GPC	gel permeation chromatography
HVAC	heating, ventilating and air conditioning system
IARC	international agency for research on cancer
ICOM	international council of museums
JND	just noticeable difference
LSD	least significant difference
MANOVA	multivariate analysis of variance
NICHE	new risk assessment methodology for cultural heritage protection
NIR	near-infrared
PCA	principal component analysis
PCC	precipitated calcium carbonate
PLS	partial least square
TCF	total chlorine free
SEC	size exclusion chromatography
SEM	scanning electron microscopy
XRF	x-ray fluorescence

LIST OF SYMBOLS

a	constant in the Mark-Houwink-Sakurada equation
$\mathbf{a^*}$	colour coordinate (red-green axes)
A	frequency factor
ANR	non-recycled Arcoprint paper
$\mathbf{b^*}$	colour coordinate (yellow-blue axes)
d	tolerance
$\Delta\mathbf{E}$	colour difference
$\Delta\mathbf{E^*_{ab}}$	colour difference formula CIE 1976
$\Delta\mathbf{E_{00}}$	colour difference formula CIEDE 2000
DP	degree of polymerisation
$\mathbf{DP_0}$	initial DP value
$\mathbf{E_a}$	activation energy
$[\boldsymbol{\eta}]$	intrinsic viscosity
$\boldsymbol{\eta}_\mathbf{r}$	viscosity ratio
HW	hardwood
k	rate constant
$\mathbf{K'}$	constant in the Mark-Houwink-Sakurada equation
l	number of unbroken glycosidic bonds
$\mathbf{L^*}$	colour coordinate (lightness axes)
LODP	levelling-off DP
M	number of chains
$\mathbf{M_n}$	number-average molar mass
$\mathbf{M_v}$	viscosity-average molar mass
$\mathbf{M_w}$	weight-average molar mass
MC	moisture content
n	sample size with the finite population correction
$\mathbf{n_0}$	sample size
N	number of monomers
$\mathbf{N_p}$	population size
NW	non-wood
$\mathbf{P_v}$	water vapour pressure

R	gas constant
RH	relative humidity
SW	softwood
t	time
T	temperature
TR	tearing resistance
TS	tensile strength
TSF	tensile strength after folding
$\mathbf{W_R}$	recycled Woodstock paper
Z	value for chosen confidence level

PREFACE

Paper is still regarded as the most widespread information carrier, despite the proliferation of electronic media. As in all other organic materials, degradation processes occur in paper-based materials. In a general sense, degradation relies on various factors that influence how fast it proceeds and which properties are affected. The modern approach to degradation studies of such materials is increasingly focused on the knowledge of the intrinsic relationship between paper properties and environmental storage conditions. Indeed, the rates and mechanisms of paper degradation are a function of numerous parameters, mostly depending on paper properties (e.g., pH, sizing, pulping processes) and storage conditions (e.g., temperature, humidity, microorganisms).

Although the processes in the papermaking have radically changed over the centuries, the paper produced centuries ago and that currently produced can be considered, in general terms, as the same product. Paper can be defined as thin sheets or leaves made of various fibrous materials (e.g., rags, straw, wood) macerated to obtain individual filaments, then mixed with water, and potentially other substances. Nevertheless, studies of its degradation must account for the variability and different quality of paper associated with the developments in the papermaking technology over the centuries. It is well known that different types of paper can degrade with different rates. The chemical and physical properties of paper mainly result from the fibrous material, pulping process, sizing components, and additives used in its production. The paper produced from rags in the 16th century is generally more stable than that produced from wood fibres in the 20th century. Substantial changes in the papermaking also includes the more recently increased use of recycled fibres, as encouraged by environmental and economic reasons.

This is the broad context in which the present doctoral thesis is set. This thesis is concerned with kinetics and effects of paper degradation, investigating this undesired, but inevitable, process from three different points of view. The first aspect that this work investigates is concerned with the comparison between the degradation rates of recycled and non-recycled contemporary paper, to understand whether and how they differ. Secondly, combining findings recently reported in the literature on the characterisation and degradation of historical paper, the data supplied by a non-destructive survey of the collections of an historical Italian Library are elaborated to model different scenarios for their preservation. Finally, the effects of γ-irradiation as a treatment for mass disinfection against fungi and microorganisms are evaluated.

The presentation of this thesis work is divided into four chapters, each one with its own abstract.

Chapter 1 discusses a general background on the issue of degradation of paper-based materials, with emphasis on the topics directly involved in this work.

Chapter 2 deals with the kinetics of degradation of virgin non-recycled and recycled contemporary paper evaluated by degrading paper samples at various conditions of temperature and humidity.

Chapter 3 reports on the characterisation of historical book collections housed in the *Classense Library* of Ravenna (Italy), predictions of their degradation rates in different scenarios achievable in various environmental storage conditions.

Chapter 4 treats the effects of degradation due to the use of γ-irradiation as a treatment for mass disinfection against fungi and microorganisms.

CHAPTER 1

GENERAL BACKGROUND

Abstract

The first part of this Chapter gives an outline of the main steps in the papermaking history, dwelling upon the aspects connected with the three lines of research of the present doctoral thesis. Understanding the changes in paper manufacture allows to evaluate the corresponding changes in paper properties and mechanisms which affect the ageing behaviour. Since paper invention, papermaking technology underwent various developments, but the real turning point from the perspective of paper degradation can be traced back to the mid-19th century, when important changes were made to manage the ever-growing demand for paper. The introduction of wood fibres as a source of fibrous material, the consequent need of implementation of chemical processes able to delignify and/or bleach the pulps, and the introduction of new sizing agents rendered the paper produced between 1850 and 1950 more acidic and susceptible to degradation processes. Over the last decades, acid-free paper, bleached without elemental chlorine or totally chlorine free, has been increasingly available. It is also to be noted that the papermaking technology is currently changing, mainly to respond to economic and environmental issues. Recycled paper is increasingly produced, especially in Europe. Therefore, the main features and properties of historical and contemporary papers are discussed, paying attention to their fibrous and non-fibrous components.

The second part of this Chapter outlines the main degradation mechanisms and most common methods to investigate paper degradation. Degradation reactions may affect all

paper components, fibrous and non-fibrous. However, this doctoral thesis focuses especially on the degradation of cellulose, as it is the main constituent of paper. Attention is also devoted to the description of techniques mainly involved in cellulose degradation studies, from accelerated ageing experiments and viscometric measurements to the calculation of rate constant and activation energy through the kinetic model of the acid-hydrolytic degradation.

1.1 A history still changing

The most ancient materials upon which hieroglyphics and characters were incised or inscribed were rocks, ceramics, leaves, bark, cloth, papyrus and parchment [1]. The demand for more practical writing surfaces derived from the invention of camel-hair brushes and fluid pigments. Paper invention is historically dated back to 105 AD[1], and attributed to the Chinese Ts'ai Lun. He is credited with reducing fibrous matter (likely mulberry and other barks), although it has been shown that Ts'ai Lun only perfected and improved a technique already known [2]. This invention, widely used in China, spread and got established worldwide as a writing surface. Around 300 AD papermaking spread across eastern Turkestan, where paper made from rags and barks, with improvements in sizing with pastes made from grains, became of general use in 450 AD. In 610 AD papermaking was introduced into Japan from China. Since 700 AD, a few papers had begun to be sized, first with gypsum, followed by glue or gelatine made from lichen, then starch, flour and other sizing agents derived from grains. In 707 AD, the earliest use of paper at Mecca was recorded, and in 800 AD in Egypt, probably imported from Samarkand or Baghdad. At the end of the 9th century, paper gradually started replacing papyrus as the major writing medium in Africa[2]. Following these early stages of paper diffusion by Arabs, around 1000, paper made from linen and hemp rags with starch appeared in Europe and in 1151 the first European stamping-mill was established in Xátiva, Spain, this type of mill being used until the invention of the Hollander beater. The first mention of a paper mill in Italy is dated 1276 at Fabriano, followed by a paper mill in Bologna in 1293. Since then, paper mills were established across Europe, in France at Troyes in 1348, in Germany at Nuremberg in 1390, in Flanders and Switzerland in 1405, in Poland in 1491 and in England at Hertfordshire in 1495 [1].

In medieval times, paper consisted primarily of beaten, soaked and macerated linen, cotton becoming also an important component. In Europe, the papermaking processes, which basically consisted in the production of pulp and its conversion into paper, were slow and manual [3], with a rigorous division of the tasks amongst the beaterman, vatman, coucher, layer and the sizeman [4]. The fibrous retted materials were manually pulped using

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[1] It is worth noting that this date was chosen rather arbitrarily as the first experiments in papermaking were probably carried out long period before that the process was perfected and publicly announced [1].

[2] This radical change in the diffusion of paper as writing material can be supported by the closing words of an Egyptian letter dated between 883 and 895: «Pardon the papyrus» [1].

mortar and pestle, only later mechanically using stampers. In Europe, the pulping process was often performed using hard water, containing lime, which contributed to the alkalinity of the resulting product [3]. Moreover, as the resulting sheet of cellulosic fibres was water absorbent, starch and flour were added to the pulp until the 13th century, when the use of gelatine sizing on an already formed sheet was introduced [5]. Indeed, the earliest use in Europe of animal glue sizing for paper is dated back to 1268-1276 [6]. It was applied by dipping the paper in a solution of gelatine [3], but as any protein, it was subjected to biodeterioration, quickly degrading at ambient temperature and in the presence of moisture [4]. Gelatine sizing did not change much until the 17th century, when the use of alum with gelatine size in the West was reported [3]. Alum (potassium aluminium sulphate) up to 5% by weight was introduced mainly to reduce the rapid biodeterioration, but it had also additional properties, binding gelatine and paper, preventing newly sized sheets from adhering to each other, and controlling the viscosity of the size [4]. Some negative effects in terms of durability of alum-sized paper were noted, as in the presence of water, alum gives rise to acids, decreasing the pH of the sized surface. However, the gelatine sizing and the use of alum persisted until well into the 19th century. Throughout the 13th to the 18th centuries papermaking practices underwent further modification stages as the production increased due to the economic expansion, feeding an ever-growing demand for paper. Indeed, since the invention of the metal movable type printing in 1450-1455 in Europe, the demand for paper extremely increased, more than 10 million of books, called *incunabula*, being produced from that date until 1500 [5]. The constantly increasing demand for paper soon resulted in attempts and efforts to speed up the papermaking processes and to explore new fibrous sources than linen and cotton. The invention of the Hollander beater brought forth much faster and productive processes than mechanical stampers, though its pulping action resulted in shorter fibres [3]. The earliest suggestions for a papermaking material that might have been substituted for linen and cotton occurred in 1684, when Edward Lloyd discussed his impracticable plan of making paper from asbestos. Early significant attempts to use new fibre sources should be dated back to the 18th century with the observations and experimental works of Réaumur, Guettard and Schäffer. In 1719 René Antoine Ferchault de Réaumur suggested the use of wood after studying wasps in making their nest [1]. In 1741, Jean Étienne Guettard advocated the use of filamentous algae (conferva) and other forms of vegetation as suitable material for papermaking. Between 1765 and 1772 Jacob Christian Schäffer made use of more than eighty different vegetable fibres with a mixture of linen and cotton in the fabrication of paper. Nevertheless, in that period practically all paper of occidental origin was made from linen or cotton rags, or a mixture of these fibres [1].

Although the important pioneer efforts to discover new papermaking fibres in Europe, radical changes to respond to the constantly increasing demand for paper occurred in the 19th century with the experiments of Koops and Keller. These changes constitute the real turning point in the papermaking, especially concerning the durability of the resulting paper. Indeed, although the 1794 invention of the cotton gin made much greater amounts of cotton fibre available, it became more and more difficult to provide enough fibres and rags[3] to cope comparatively with this fast-growing demand. The exigency of developing other fibre sources grew especially with the introduction of the Fourdrinier machine, which converted the paper production from batch into continuous [3]. In this regard, the work of Matthias Koops has been considered as responsible for the growth of the paper industry as it is today [1]. In 1800 and 1801, Koops was granted three patents: the first one for the extraction of printing and writing ink from paper before repulping, the second and the third ones covered the manufacture of paper from straw[4], hay, thistles, waste and refuse of hemp and flax and different kinds of wood and bark [1]. Then, in 1840 Friedrich Gottlob Keller secured a German patent for a wood-grinding machine. Keller defibred blocks of wood by pressure against a revolving wet grindstone, then adding a percentage of rag fibres to strengthen the paper. While the ground-wood process gave the paper industry a cheap paper in huge amount for various uses, there was still the necessity for a more durable and lasting paper at intermediate cost between the paper made from groundwood and that made from rags. Since the early decades of the 20th century, as the demand for paper kept growing and the textile materials were no longer able to satisfy that demand, wood became increasingly used.

In parallel with the replacement of fibrous materials, other processes such as pulping, bleaching and sizing changed as well. In 1774 Scheele's discovery of chlorine led soon to the introduction of chlorine bleaching with its diffusion in the 19th century. All paper made before assumed the tone of the material from which it was made [1], although in medieval times practices involving boiling with lime, for instance, had some bleaching effects [2]. In 1785, Claude-Louis Bertholette experimented gaseous chlorine, but the

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[3] It was fairly common to find in periodicals of that time, in both Europe and America, advertisements which implored the population to «Save Your Rags» [1].

[4] Koops published a book printed on paper that he made by his own process from straw, with also a few leaves of paper made from wood [1].

diffusion of wood pulp in the papermaking industry brought forth the exigency of bleaching processes applicable at an industrial level. Later, it became common the hypochlorite process, then replaced due to its environmental impact by peroxide, ozone and enzymatic processes in the last decades. Elemental chlorine free (ECF) and total chlorine free (TCF) papers are currently widely produced.

The invention of rosin[5] sizing for paper by Moritz Friedrich Illig in 1807 [6], represents a substantial change in the chemical properties of the resulting paper, decreasing its durability. In the mid-19th century, for the control of water penetration, potassium aluminium sulphate was replaced by aluminium sulphate, also known as papermakers' alum, given that the latter was more easily available on an industrial scale [4] and assisted the flocculation of colloidal particles behaving as a mildly effective retention aid. Therefore, from the early 19th until well into the 20th century, rosin sizing was added to the pulp and precipitated with papermakers' alum, causing a significant acidity increase of the resulting paper [5].

Furthermore, the use of wood as cellulose source favoured the implementation of chemical processes in papermaking for elimination of components such as lignin and hemicelluloses. In 1851 Hugh Burgess and Charles Watt were able to produce the first useful paper made from chemical wood fibre [1]. It basically consisted in pulp production by boiling wood in caustic alkali at high temperatures, referred to as soda process. A pioneer in another chemical process for the preparation of wood fibre for papermaking was Benjamin C. Tilghman who made a suitable wood pulp for paper by involving the sulphite method, an acidic process [1]. It included the application of sulphurous acid, kept at high temperatures and pressures. Improvements in the steam boiler technology by Carl F. Dahl in 1884 brought forth the sulphate process [1]. In other words, acidic processes were generally implemented, which together with the use of alum-rosin, led to the production of very acidic paper, its permanence and durability being thus significantly affected. In this regard, as reported in Chapter 3, the results of an innovative condition survey conducted on an historical Italian collection, which is dated between the 14th and 20th century, are in line with this sharp decrease of paper pH over that period. Actually, since the early attempts to use fibres other than linen and rag, the papermakers seemed to be aware that the resulting products were not as good as paper made from cotton in terms of durability.

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[5] Rosin is also known as colophony from its origin in Colophon, an ancient Ionic city [7].

Over the last decades, changes in the papermaking technology have addressed concerns about the durability of the resulting paper and environmental impacts due to paper production. Since the 1990s acid-free paper has been produced, neutral or alkaline processes being increasingly implemented along with the use of fillers (e.g., calcium or magnesium carbonate) as alkaline reserve. Currently, fibrous materials mainly derive from wood, non-wood (e.g., straw, bamboo, bagasse) and paper for recycling [8]. Mechanical, semi-chemical and chemical pulps are the three main types of wood pulp, different depending on the processes involved, most of the wood pulp being currently produced using chemical pulp. Mechanical pulps, obtained by grinding or milling wood chips into relatively short fibres, simply involves the conversion of raw wood into pulp without any removal of lignin. Until the second half of the 20th century, mechanical pulps had been produced by the stone-ground wood process, where blocks of woods were pressed against an abrasive rotating stone surface. After that period, refining processes in which the wood is introduced into a disk refiner via a screw feeder became increasingly common. Sometimes, the wood is steamed under pressure for a short period to soften the chips, reducing the shortening of the fibres[6] [9]. This is now one of the major processes for the production of newsprint [8]. Semi-chemical pulps are obtained by subjecting wood chips to a series of mechanical treatments, and cooking them in a pressure vessel, none of which alone being sufficient to separate the fibres. This pulp is mainly used in the production of fluting medium for corrugated boards [8]. The mechanical and semi-chemical pulping processes remove very little lignin, more extensive lignin removal being based on aqueous and high temperature extraction procedures at acidic, neutral or alkaline pH, namely chemical pulping [9]. Indeed, chemical pulp is obtained performing a series of chemical treatments which include sulphate (also known as kraft), soda and sulphite wood pulp. Organic solvents can also be used, the main problem for their large-scale diffusion being related to their recovery. The ideal chemical pulping process should render the lignin soluble for its extraction without causing degradation to the carbohydrate components. For this reason, the severe acidic conditions, although still in progress, have largely been replaced over the past 50 years by neutral and alkaline processes. Alkaline delignification, in the form of kraft process, is currently a widely used method for the production of papers with different end-uses (e.g., graphic papers, tissue, bag papers), whereby a mixture of

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[6] Thermo-mechanical Pulp (TMP) is produced by a mechanical process in which wood chips are softened by pre-heating under pressure prior to a pressurised refining stage.

sodium hydroxide and sodium sulphide is used, the latter being produced in the recovery process by the reduction of sodium sulphate [9]. By leaving out sodium sulphide, and only using sodium hydroxide as the cooking chemical, the process is called soda cooking. Besides, sulphite pulping involves cooking wood chips in a pressure vessel in the presence of a bisulphite cooking liquor, ammonium, calcium, magnesium and sodium being commonly used [8]. Although it usually occurs in acidic environment, appropriate bases can be used to control pH, these reactions being performed even at neutral or alkaline pH [9]. End-uses of paper produced with sulphite process range from newsprint, printing and writing paper, tissue and sanitary papers [8].

As far as the effects of chemical delignification on the carbohydrate fraction are concerned, that of pH is predominant. Degradation in alkaline and acidic pulping environments should therefore be considered separately. In brief, the most important degradative process in alkaline pulping is the so-called peeling reaction, in which single monosaccharide units are sequentially removed from the reducing end of the chain, both cellulose and hemicelluloses being affected [9]. The reducing end of the polysaccharide isomerises to the ketonic form with consequent cleavage of the glycosidic linkage. The product thus shortened by one glucose residue may undergo further degradation. As it is a sequential reaction, the DP of carbohydrates is reduced but not as severely as in a random process. The so-called stopping reaction, much slower than that of peeling, controls the extent to which the latter occurs. Cleavage of internal glycosidic bonds of cellulose probably due to alkaline hydrolysis reaction can also occur at very high temperatures, leading to formation of 1,2-epoxides [9]. On the contrary, the main effect of high temperature and low pH is the hydrolysis of glycosidic bonds in the polysaccharide chains, as discussed in more detail below. This process does not seem to be selective to the chain end but occurs relatively randomly along the polysaccharide backbone [9]. Because of the cellulose insolubility even at very low degrees of polymerisation (DPs), significant depolymerisation may take place without significant solubilisation. However, the depolymerised pulp is considerably weakened, and this probably accounts for the different strengths of pulps from acidic or alkaline processes. Hemicelluloses are the molecules most susceptible to hydrolysis at this stage, which probably accounts for the lower levels of hemicelluloses in acidic pulps.

However, since the early 1970s, the tendency toward neutral and alkaline pH had a substantial effect also upon the whole of the chemistry of the aqueous fibre suspension, for instance the type of sizing because of their high sensitivity to pH. The need to produce alkaline paper led also to the development of synthetic compounds for sizing [9].

As mentioned above, in addition to wood and non-wood (e.g., straw, bamboo, bagasse) materials, paper for recycling [8] is to be considered, the use of recycled fibres being steadily increased. The use and ever-growing levels of recycled fibres as source for papermaking can be attributed to environmental and economic reasons. Recycling of paper is generally considered to be environmentally beneficial, although the environmental arguments are not as straightforward as it might be imaged [9]. However, even if consumer pressure to recycle is increasing, in Europe the ever-growing recycling levels can be also attributed to economic reasons, recycled fibres being an important cheap and readily available resource in a continent where wood is in short supply. On the contrary, in countries such as those in North America, recycling has not been an economic necessity. Nevertheless, consumer pressure has been responsible for a significant increase in recycling over the last few years, but still at a much lower level than in Europe [9]. It is impressive that the recycling rate[7] in Europe grew in the last decades, going from 40.3% in 1991 to 72.3% in 2017 [10]. The quality of paper made from recycled fibres is generally considered to be lower than that from non-recycled (virgin) material, but the behaviour of different types of pulp can be very variable [9]. The difference from a kinetic perspective between recycled and non-recycled paper will be addressed in Chapter 2.

1.2 Paper properties and components

Although paper was invented and spread across the world as a writing medium, it has been produced for various end-uses with essentially the same processes. It is thus possible to describe the paper in terms of its method of production, whereby a sheet material is made up of a network of cellulosic fibres which have been deposited from an aqueous suspension [9] with the possible addition of other components.

Nowadays, the basic raw materials to produce pulp and paper can be split into two parts: fibrous and non-fibrous materials [8].

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[7] Ratio between recycling of used paper, including net trade of paper for recycling, and paper and board consumption [8].

1.2.1 Fibrous materials

The fibres of which paper is made are the structural cells of plant, which may derive from wood, non-wood fibre sources or, alternatively, paper for recycling [8]. Wood and paper for recycling are currently the main fibre sources used in Europe. Two broad wood-species are used: hardwood and softwood. The former come from non-coniferous trees, classified as angiospermae, the most used hardwood species for papermaking being birch, eucalyptus, beech and aspen, while the latter include coniferous trees, classified as gymnospermae, the most used softwood species being pine and spruce. Hardwood and softwood have very different fibre morphologies, thus accounting for different papermaking properties. Softwood fibres are longer and stronger than those of hardwood, and constitute the bulk of papermaking fibre worldwide, about 73% of the total wood pulp deriving from softwood and the remaining 27% from hardwood [10].

The fibrous portion of the resulting paper may have different chemical compositions depending on the fibre source. These fibres are mostly composed of carbohydrate polymers which can be impregnated to various extents with lignin and other components (e.g., resins). The major structural component of the fibres, and consequently of the resulting paper, is cellulose. Other polysaccharides with non-structural functions, and very lower molecular weights than that of cellulose are known as hemicelluloses. Table 1.1 reports the distribution of the three main components along with other trace materials in softwood and hardwood.

Table 1.1. Distribution of the main chemical components of softwood and hardwood fibres [9].

	Cellulose (%)	**Hemicelluloses (%)**	**Lignin (%)**	**Extractives and traces materials (%)**
Softwood	40-45	20	25-35	<10
Hardwood	40-45	15-35	17-25	<10

Softwoods are composed of two kinds of cells: longitudinal tracheids and ray parenchyma, with the first ones occupying about 90-95% of the wood volume. Tracheids are the principal papermaking cells, their average length ranges from 2 to 6 mm, length and width varying within and between species. Softwood cells are equipped with pits, and water conduction between tracheids takes place through bordered pits. The pits in the crossings of the tracheids and the ray cells are called cross-field pits. Their size, shape and arrangement allow to distinguish between windowlike, pinoid, piceoid, cupressoid, taxodioid pits, being thus possible to identify the various species (e.g., cross-field pitting is the most important feature in the identification of softwood species in pulp) [11].

Hardwoods have a more advanced and complex structure than softwoods. Special types of cells have been developed from tracheids, that are vessel elements for conduction and fibres for support. These vessel elements together with parenchyma compose the main parts of hardwoods and are present in all species. Vessels allow to identify hardwood species, being the only cell type showing constant structural variations between different genera. Because of this, the identification of hardwood is based mainly on the features of vessel elements [11].

The identification of different wood genera is usually possible, while the identification of individual species is often difficult or even impossible, as species of the same genus may be closely related in anatomical structure. The degree of success in identification relies on a number of factors such as the present species, pulping, bleaching and beating processes. It may be difficult to find intact cross-field pits or vessels in highly beaten pulps [11]. Figure 1.1 shows the differences between the anatomical structures of softwood (*Pinus sylvestris*) and hardwood (*Betula verrucosa*) fibres.

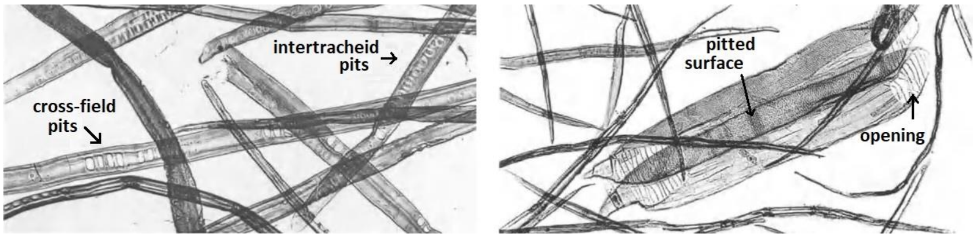

Figure 1.1. Left: Softwood (Pinus sylvestris) sulfate fibres showing intertracheid pits (T) and large windowlike cross-field pits (CF), 100x. Right: Hardwood (Betula verrucosa) pulp showing vessel elements and fibres. o = opening with ladderlike bars between two vessel elements, p = pitted surface between two vessel elements, 100x. Adapted from [11].

As mentioned above, chemical treatments are implemented during the conversion of fibres into pulp. In case of mild or no chemical treatments (e.g., mechanical pulp), the chemical composition of the resulting paper is very similar to that of native wood [9]. Table 1.2 reports the chemical composition of three native woods, softwood (spruce and pine) and hardwood (birch), along with that of the pulp derived using the sulphite and kraft pulping processes.

Table 1.2. Chemical composition (%) of hardwood (HW) and softwood (SW) species, and pulp derived with sulphite and kraft processes [9].

Pulping process	**Tree species**	**Cellulose (%)**		**Hemicelluloses (%)**		**Lignin (%)**		**Extractives (%)**	
		Wood	Pulp	Wood	Pulp	Wood	Pulp	Wood	Pulp
Sulphite	Spruce (SW)	41	78.1	30	17.1	27	3.8	2	1.0
	Birch (HW)	40	81.6	37	12.2	20	4.1	3	2.1
Kraft	Pine (SW)	39	73.3	30	18.9	27	6.3	4	1.1
	Birch (HW)	40	63.6	37	31.8	20	3.7	3	0.9

Non-wood fibres are important especially in those regions where the use of indigenous raw materials can reduce the costly amount of imported wood pulp. The main advantage of these fibres, such as straw, bamboo, bagasse, cotton, is that they generally produce an annual crop with higher yields than wood in areas where the growth of trees is not well supported. The cellulose content of non-wood fibres used for papermaking, such as bagasse, bamboo, straw, is comparable to that of wood fibres, while a higher content can be found in flax or hemp, and even higher in cotton[12]. On the other hand, the lignin content of non-wood fibres is much lower than that of wood fibres, delignification of non-woods being relatively easy [13]. Table 1.3 lists the chemical composition of some non-wood fibres in comparison with that of some wood fibres, both commonly used in papermaking.

Table 1.3. Chemical composition (%) of non-wood (NW), softwood (SW) and hardwood (HW) fibres [13].

	Holocellulose (%)	**Hemicelluloses (%)**	**Lignin (%)**
Straw (NW)	78	24	18
Bagasse (NW)	78	28	21
Bamboo (NW)	77	20	23
Eucalyptus (HW)	74	18	26
Birch (HW)	81	40	19
Spruce (SW)	71	27	29

1.2.1.1 Cellulose and its properties

Cellulose was chemically identified from plants in 1838 by Anselme Payen [14,15]. He showed that plant tissues yielded a resistant fibrous substance, drawing the conclusion that it was made of a uniform chemical substance: a carbohydrate composed of glucose residues, and isomeric with starch. This substance was named cellulose by the French Academy in 1839 [15].

Cellulose is the major structural component of the fibrous material, and provided that delignification of wood pulp is effective, it is also the main structural component of paper. As showed in Table 1.2, cellulose accounts for the majority of pulp compositions.

Regardless of the source, cellulose is a linear homopolysaccharide, composed of D-glucopyranoside ring units linked by β-1,4-glycosidic bonds [12]. As shown in Figure 1.2, strictly speaking, cellobiose is the repeating unit[8].

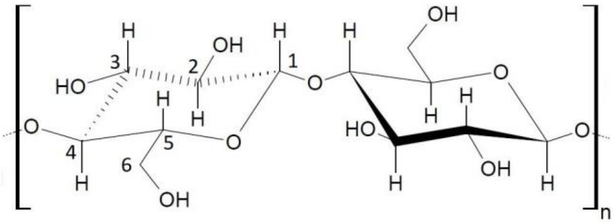

Figure 1.2. Molecular structure of cellulose as polymer of cellobiose. Adapted from [5].

Cellobiose consists of two anhydroglucose units, in which every unit is rotated by approximately 180° relative to its neighbour, both adopting a stable $^1C_4$ chair conformation [16]. The chain thus assumes a highly extended conformation exhibiting two-fold symmetry. The length of the macromolecular chain is defined by the number of monomers. It is typical to find chains with different lengths, so that cellulose materials are usually described in terms of average length of the macromolecules and their distribution. In this regard, the degree of polymerisation of a chain is defined as the number of monomers that a chain contains. One of the most cited and used chemical properties describing cellulose is the average degree of polymerisation (hereinafter referred to as DP) that is defined as the total number of monomers divided by the number of cellulose chains. Native cellulose has different DPs, that can range from 1000 to 30000 [12]. This depends on the various origins, highest DP values being generally measured in native non-wood source (e.g., flax, cotton). As mentioned above, cellulose is a polydisperse molecule, and also its polydispersity depends on the source of cellulose, cotton and linen cellulose being less polydisperse than wood cellulose. As a consequence, DP values of cellulose in paper materials vary considerably as a function of the origin of the fibres, purification procedure (such as delignification) and degradation mechanisms (such as hydrolysis) [12]. In paper

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[8] It is to be noted that DP is calculated considering the glucose as repeating units.

degradation studies cellulose is typically described in terms of average molar mass and average DP.

As shown in Figure 1.2, there are three hydroxyl groups in each anhydroglucose unit, a primary group at C6 and two secondary groups at C2 and C3 [12]. Cellulose chains are also characterised, as other polymers formed by polycondensation, by a reducing end with a D-glucopyranoside ring in equilibrium with the corresponding aldehyde function, and a non-reducing end with an anomeric C atom linked by the glycosidic bonds [12]. This structure accounts for some peculiar properties of cellulose, namely, highly hydrophilic character, corresponding high surface energy, biodegradability, and marked reactivity associated with the three hydroxyl groups present in each anhydroglucose. Cellulose is also characterised by hydrophobic areas, around the C atoms. These properties are also detectable in other polysaccharides (e.g., starch, hemicelluloses), although cellulose remarks a stronger tendency to crystallise through a regular network. The presence of hydroxyl groups and oxygen atoms on the pyranose rings promotes systems of hydrogen bonds, which contribute significantly to determine its limited solubility in most solvents, reactivity of the hydroxyl groups and crystallinity. The first studies in the 1920s on the crystal arrangement of cellulose molecules in the crystallites classified both native and modified cellulose on the basis of their X-ray diffraction patterns. Although cellulose exists in four polymeric forms, referred to as cellulose I, II, III and IV, only cellulose I occurs naturally, even if this is not the most stable form [16]. As discovered by VanderHart and Atalla [17], native cellulose (cellulose I) has a crystalline dimorphism. Cellulose I is thus composed by two polymorphic forms, Iα and Iβ, present in variable percentages depending on the cellulose source: Iα, a triclinic structure enriched in most algae and bacteria, and Iβ, a monoclinic structure dominant in higher plants [18]. The percentages of crystallinity range from 50 to 90% depending on the source, for instance cotton tending to be more crystalline than wood [9]. It has been shown that crystalline areas can prevent access of gases and liquids to cellulose chains, and consequently they prevent reactants from reaching the chains for degradation. It is well documented that cellulose in paper is a semi-crystalline material, in which the amorphous regions are more reactive than the crystalline ones [19].

Intrachain H-bonds in cellulose Iβ are thought to occur between O(3)–H···O(5) and also between O(2)–H···O(6), while O(6)–H···O(3) interchain H-bonds are formed at different chains in the same sheet. The intrachain hydrogen bonding is dominated by the strong O(3)–H···O(5) bond, the most agreed upon in the literature, less consensus being found on other bonding configurations. Figure 1.3 shows inter- and intramolecular hydrogens bonds in cellulose.

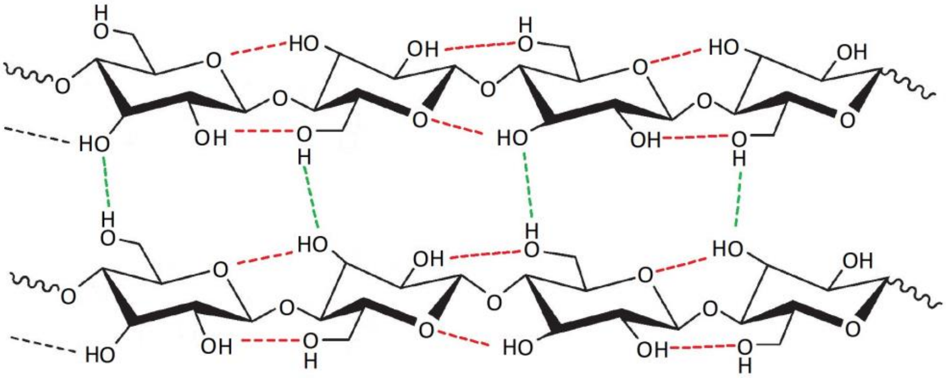

Figure 1.3. Pattern of inter- and intramolecular hydrogen bonding in cellulose. Adapted from [20].

Intramolecular hydrogen bonds have several functions in cellulose. They assist in maintaining its highly extended conformation allowing to function as a structural polymer [9], are responsible for the rigidity or stiffness of the cellulose polymer, and lead to a tendency to crystallise or form fibrillar structures [12]. On the other hand, intermolecular hydrogen bonds are responsible for the strong interaction between cellulose chains. Overall, hydrogen bonding, weak C–H–O bonds, and hydrophobic interactions around C atoms account for the arrangement of cellulose in layers [12], as elucidated by synchrotron X-ray and neutron diffraction experiments [21]. Different structural levels form the typical hierarchical morphology of the plant cellulose fibres, as shown in Figure 1.4.

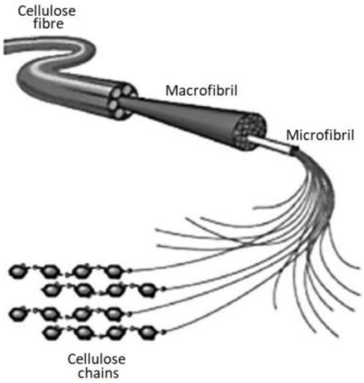

Figure 1.4. Hierarchical morphology in a plant cellulose fiber. Adapted from [22].

Cellulose chains are assembled as the so-called elementary fibrils[9], which have been reported to have a length of 100 nm and a characteristic lateral dimension of 1.5-3.5 nm [23]. Such elementary fibrils are arranged as the so-called microfibrils, with widths that can vary between 10-30 nm, themselves grouped into larger aggregates called macrofibrils 100-

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[9] It is to be noted that other authors consider a microfibrils as consisting of a number of elementary fibrils.

400 nm wide. In plant cell walls, a sheath of amorphous cellulose, which is surrounded by hemicelluloses, further covers microfibrils [12]. It has been also reported that in wood fibres, hemicelluloses and traces of lignin are involved in the microfibrillar arrangement at the periphery of the well-ordered cellulose chains [4]. As the cell grows the macrofibrils may thus split to form individual microfibrils consisting of single elementary fibrils associated with non-cellulosic polymers. Therefore, elementary fibrils and macrofibrils contain only cellulose, while microfibrils may contain both cellulose and non-cellulosic polymers [24].

In other words, three organisational levels can be described: a molecular level, determined by molecular composition and intramolecular hydrogen bonding; a supramolecular level, associated with intermolecular hydrogen-bonding and aggregations of macromolecules into elementary fibrils; a morphological level, related to the superior level of organisation from elementary fibrils to fibres and cell layers [4].

As mentioned, cellulose is a semi-crystalline material with regions of high micro-crystallinity and amorphous regions, as shown in Figure 1.5. The spatial distribution of amorphous domains within an elementary fibril is not resolved, models of crystalline cores surrounded by amorphous shells at its surface, and of alternating crystalline and amorphous domains along the fibril being suggested in the literature [22,24].

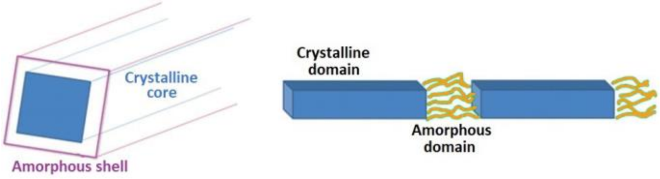

Figure 1.5. Possible structures of elementary fibrils. Adapted from [24].

1.2.1.2 Hemicelluloses and lignin

In cell plants, cellulose is usually accompanied by other components such as hemicelluloses and lignin. Especially, in wood fibres, as mentioned, hemicelluloses and lignin may be involved in the microfibrillar assembly [4]. These components are mostly removed during pulping processes, although small amounts may be still present after the pulp is generated.

Hemicelluloses consist of a mixed group of non-structural heteropolymers including C5 and C6 monomeric residues. Indeed, they are usually based upon the hexoses D-glucopyranose, D-galactopyranose, D-mannopyranose, 4-O-methyl-D-glucuronic acid, the pentoses L-arabinofuranose and D-xylopyranose. As cellulose, these polymers are formed by condensation with the removal of water molecules at every linkage. All of the monosaccharides that compose hemicelluloses have the D-configuration and occur in the pyranoside forms, except arabinose, which has the L-configuration and occurs as a furanoside [25]. The structure of these monosaccharides that form the hemicelluloses is shown in Figure 1.6.

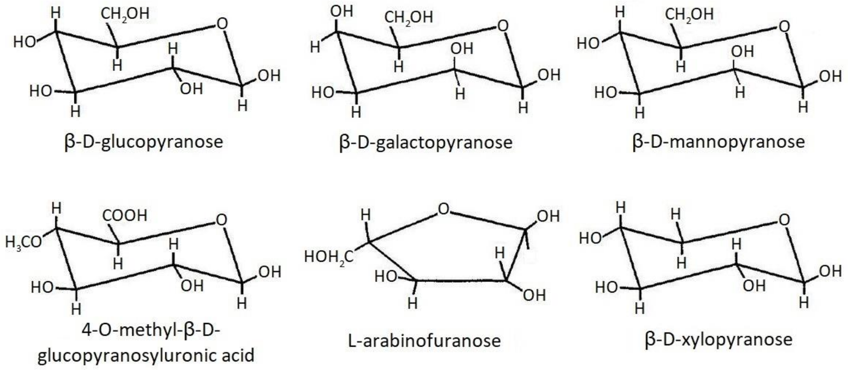
β-D-glucopyranose
β-D-galactopyranose
β-D-mannopyranose
4-O-methyl-β-D-glucopyranosyluronic acid
L-arabinofuranose
β-D-xylopyranose

Figure 1.6. Molecular structure of the main monosaccharides in wood hemicellulose. Adapted from [25].

DP values of hemicellulose range between 100-200 sugar units, considerably lower than that of cellulose molecules [25]. Not only the amount but also the hemicellulose polymers can vary with the type of fibres. For instance, the main hemicelluloses in softwood fibres are galactoglucommans, glucomanns, arabinoglucuronoxylans, and arabinogalactans, the latter only being water-soluble, and so usually classified as an extractive. At variance, the principal hemicellulose of hardwood fibres is the glucoronoxylan with a small amount of glucomannans [25]. Hemicelluloses are much more soluble and susceptible to chemical degradation than cellulose. It has been commonly accepted that they have beneficial effects on pulp and paper properties, although the reasons are not well recognised [9]. They increase the strength of paper (especially tensile, burst, and fold) as well as the pulp yield, though they are not desired in dissolving pulps [25]. In addition, as they may be expected to assist inter-fibre bonding, they are absorbed to fibre surface during pulping and mechanical refining. Given their non-crystalline hydrophilic nature, they may also contribute towards the swelling of the pulp, thus improving the conformability of the wet fibres during sheet formation [9]. Because of their solubility in alkali, hemicelluloses can be separated from cellulosic components through alkaline extraction. However, an efficient extraction is possible only if fibres have been previously delignified. This is because the covalent ester linkages, which link hemicelluloses with lignin, need to be cleaved in order to solubilise hemicelluloses. Their solubilisation may occur at the early stages of alkali pulping, but reprecipitation, and presumably return back into the cell wall, can occur later, at the end of pulping. A possible explanation of this behaviour can be related to the alkali consumption as the pulping process proceeds, and consequently to the decrease of solubility of hemicelluloses, as well as to their structural modifications, which can render the polysaccharides less soluble [9]. As a result, the content of hemicelluloses obtained from alkaline kraft pulps is higher than that of acidic sulphite pulp, as reported in Table 1.2.

Lignin is a complex aromatic polymer consisting of phenylpropane units with an amorphous three-dimensional structure. Its role at the fibre level is to be an adhesive or binder, which holds the fibres together [25]. More generally, it functions as a strengthening agent, and favours the resistance of wood towards the attack by microorganisms [9].

Chemically, three basic monomers are found in lignin: coniferyl, sinapyl and p-coumaryl alcohols [25]. Figure 1.7 shows the molecular structures of the lignin precursors in plants.

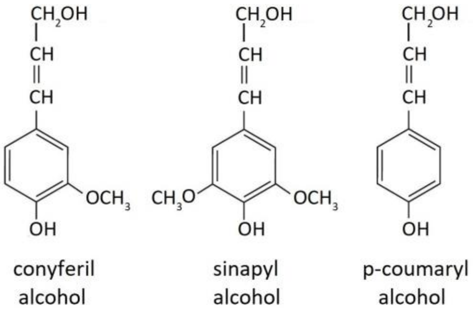

Figure 1.7. Molecular structure of the three monomeric repeating units of lignin. Adapted from [26].

However, each of these monomers contributes differently to lignin depending upon the source. For instance, softwood lignin contains only coniferyl alcohol, hardwood lignin is a mixed polymer of both coniferyl and sinapyl alcohols, while lignin of grasses and straw contains all three monomers [25]. Lignin is thought to be a cross-linked network polymer of molecular mass between 1000 and 4000 Da [7]. A simplified qualitative structural model of softwood lignin is shown in Figure 1.8.

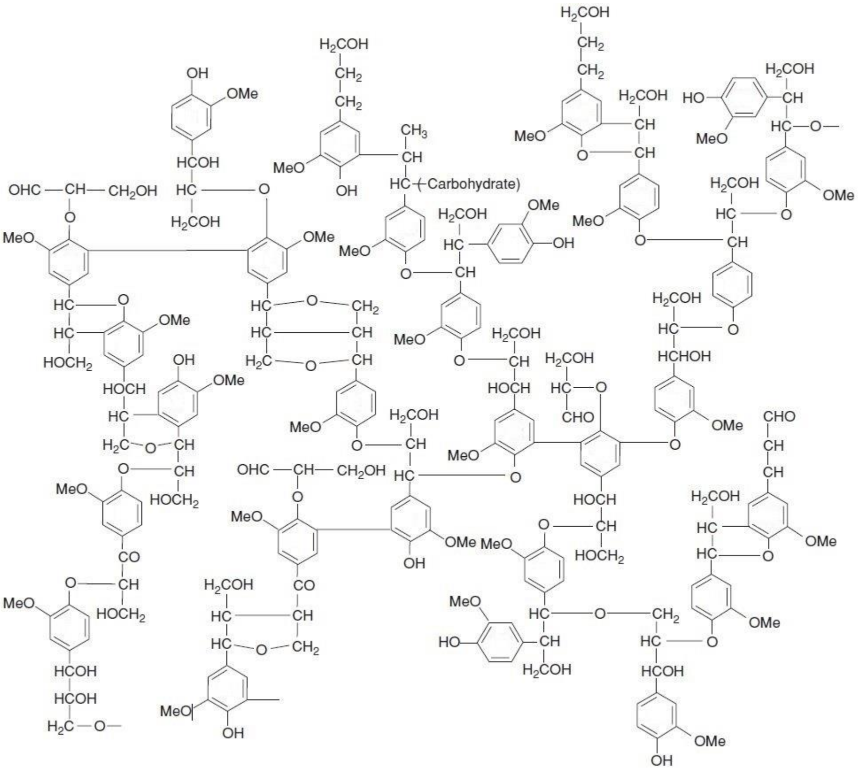

Figure 1.8. A simplified qualitative model of softwood lignin. Adapted from [26].

Because of the phenols, lignin is highly acidic and its rigid hydrophobic amorphous matrix tends to be readily oxidised. However, its hydrophobicity decreases with ageing, allowing deteriorating agents to attack cellulose and hemicelluloses. Its molecular structure makes lignin very susceptible to degradative effects of light, producing chromophoric groups by absorbing ultraviolet and visible radiation [7]. Its phenols as well as other functional groups become oxidised, then hydrolyse and can give rise to a weak acidic solution [27]. However, the role of lignin in paper degradation is not well understood, and ambiguous, as it may provide also a limited antioxidant effect [28]. As the other components, namely cellulose and hemicellulose, lignin is not uniformly distributed throughout the wood cells. The region in which lignin is most present is the middle lamella, but this is relatively small in volume, while the secondary cell wall, having a larger tissue volume than middle lamella, represents the region where most of the lignin is located. This is important given that pulping chemicals should be able to penetrate the cell wall for an effective removal of lignin. Figure 1.9 shows the distribution of the three main chemical components, namely cellulose, hemicelluloses and lignin through the cell wall.

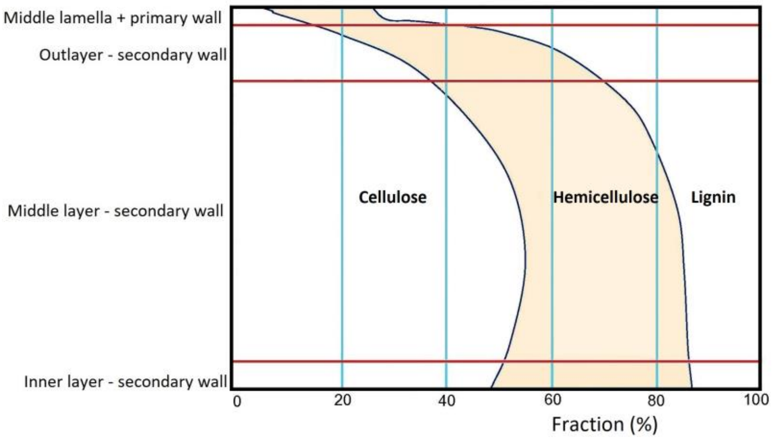

Figure 1.9. Distribution of the three main chemical components throughout the cell wall. At the top is the cell boundary and at the bottom is the interface with lumen. Adapted from [29].

1.2.1.3 Other fibrous components

Small proportions of other components can occur in non-wood and wood fibres. Pectins are a complex family of heteropolysaccharides present in the primary cell wall. Their structures vary according to the source, tissue type, developmental stage, environmental stage and conditions of extraction [30]. The pectidic polysaccharides are constituted by different structural domains. Pectins mainly consist of pectic acid, shown in Figure 1.10, a polymer of 1,4-linked galacturonic acid units, whose carboxyl functions are partly present as methyl esters [7].

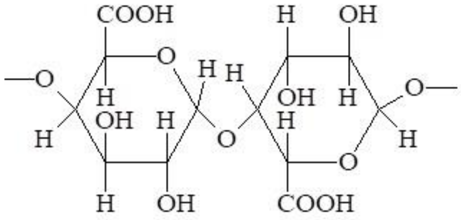

Figure 1.10. Molecular structure of pectic acid. Adapted from [7].

Other compounds, referred to as extractives as they are soluble in organic solvents, can be present with different proportions and compositions in hardwood, softwood and their species. These are compounds of various chemical nature, including alkanes, fatty alcohols and acids (saturated and not), glycerol esters, waxes, resin acids, terpene, and phenolic components [9], with low to moderately high molecular weights [25].

Given the huge variety of all the fibrous components, from cellulose and hemicelluloses to lignin and resin, their presence in the final sheet of paper depends on the source of the fibres and on the chemical pulping process involved. For instance, alkaline pulping is able to remove relatively easily acidic components (e.g., resin and fatty acids) by conversion to their soluble carboxylate salts. On the contrary, their removal through acidic pulping is not so efficient [9].

1.2.2 Non-fibrous materials

Since the early stages of papermaking, a wide variety of additives have been used for a number of reasons from aiding and assisting the efficiency of the formation process of paper to imparting desired properties to the finished paper. The Handbook of Pulp and Papermaking [31] distinguishes functional from control additives. The former ones include dyes, sizing agents, adhesives used to increase wet or dry strength, and fillers to improve other paper qualities, such as optical features, these additives needing to be retained on the paper sheet to be effective. The latter ones (e.g., biocides, retention aids) are used to improve the papermaking process and may not directly affect the resulted product, on which are not necessarily retained. However, some additives (e.g., alum) can be considered as functional and control at the same time [31].

Potential interactions between furnish components themselves and between these components and the fibrous materials may occur. In the papermaking process, in order to produce paper with the desired properties it is of great importance to take these interactions into consideration. These interactions are also extremely important to explain how and how fast paper may degrade.

1.2.2.1 Sizing agents

The term ‘sizing’ is generally used to refer both to internal and surface sizing. The former type provides resistance to water, or more in general to aqueous liquids, throughout the body of the sheet, while the latter type tries to control the penetration through the surface of the sheet. Internal sizing is thus necessarily a wet-end operation, contrary to the surface sizing that is a dry-end process [9]. As far as the internal sizing is concerned, water penetration is retarded by the non-polar portion of the size molecule, the reactive portion anchoring it to the fibre surface [31].

In the early stages of papermaking, starch derivatives, mainly derived from ground refined flours, were used. They were then replaced from the 13th to the 18th century by gelatine sizing. Gelatine is described as a mixture of peptides and proteins produced by partial hydrolysis of collagen extracted by a wide variety of raw materials, mainly animal skins and cartilage scraped from bones. The gelatine suspension was obtained by boiling, skimming and filtering the solution with raw materials and water. The paper sheet was thus immersed after adding alum, pressed to distribute the size throughout the sheet and get the excess for reuse [7]. Indeed, because of gelatine degradability especially with hot weather, to prevent the growth of mould and microorganisms, alum was added to gelatine in the mid-17th century. This could cause the formation of sulphuric acid, promoting acid hydrolysis of cellulose and thus accelerating the overall paper degradation [7]. However, from the 19th century until well into the 20th century, the most common size used was rosin with alum as precipitating agent [31].

Rosin is a mixture of a number of diterpene acids, such as abietic acid, extracted from softwood. Different complex mechanisms seem to be involved in rosin sizing, however in all of them at alkaline pH the size is poorly retained or not appropriately orientated, causing its loss [9]. As far as rosin-alum sizing is concerned, however, it is worth recalling that the term ‘alum’ is used to denote two different compounds. Historically, alum indicated aluminium potassium sulphate dodecahydrate [$AlK(SO_4)_2 \cdot 12H_2O$], while currently it is incorrectly applied to hydrated aluminium sulphate [$Al_2(SO_4)_3 \cdot xH_2O$]. The former alum added to gelatine is converted into aluminium hydroxide that acts as a crosslinking agent between gelatine and cellulose. In contrast, as a component of the acidic rosin size, aluminium sulphate acts directly as a sizing agent by precipitating rosin onto cellulose fibres and stabilising it [7]. Several theories accounting for sizing in rosin-alum system have been proposed. One of these is that rosin, reacting with aluminium sulphate, provides a reaction product positively charged, which binds the anionic cellulose at the pH of the system, thus orientating the rosin molecule onto the surface of the fibre. There are also some doubts about the type of bond between rosin, alum and the cellulose substrate, no covalent bonding being thought to be involved [9]. Figure 1.11 displays a possible mechanism, a bridge between cellulose and rosin being formed [7].

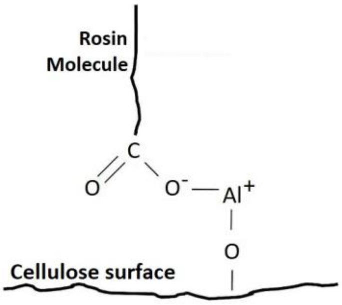

Figure 1.11. Bonding between rosin-aluminium and cellulose. Adapted from [7].

Rosin-alum sizing is considered to be one of the main causes of the chemical instability of paper produced from the second half of the 19th century, because of the resulted acidity. Alum, in fact, is hydrolysed in the presence of water, aluminium(III) hexahydrate ions hydrolyse to form hydronium ions, with *Ka* similar to that of acetic acid [32].

However, since the early 1970s there has been a move away from acidic systems towards neutral and even slightly alkaline systems. Indeed, sizing can be carried out over a wide pH range according to the size used, as shown in Figure 1.12.

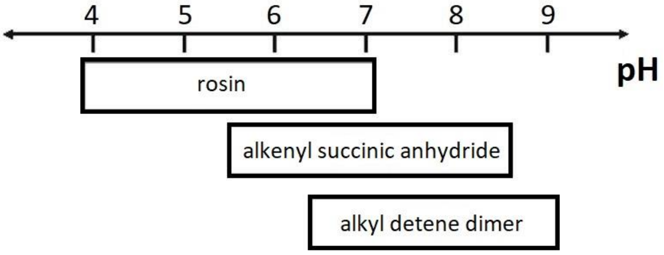

Figure 1.12. pH range of rosin, alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD) sizing agents. Adapted from [7].

Therefore, if rosin with alum is a classic example of acidic sizing, being effective only below pH 7, alkaline sizing can be carried out at pH 8 or higher using synthetic sizing agents such as alkenyl succinic anhydrides (ASA), made by reacting mixtures of C16 to C20 olefins with maleic anhydride, or alkyl ketene dimers (AKD), obtained by dimerization of the acyl chlorides of fatty acids. These agents are water insoluble, an emulsion with stabilising cationic starch being used to apply them [31]. In contrast to acidic sizing systems, the size molecule seems to undergo also covalent linkages with the hydroxyl groups of the fibres by esterification. The presence of covalent bonds assists in attaching the hydrophobic group in a highly oriented state [9].

As far as surface sizing is concerned, a very commonly used surface size, because of its cheapness, is starch, others such as carboxyl-methyl cellulose and alginates, more expensive, being also employed. Starch, an energy storage polysaccharide, had been used since the early stages of papermaking and it currently is the third most important paper furnish per weight used, considering pulp and clay the first two [31]. Actually, starch has multiple effects. It can be used not only as a surface sizing but also as a retention aid, dry strength agent and coating binder. Amylose and amylopectin are the two components of starches, each of them is present with different amounts depending on the source [31].

1.2.2.2 Strength additives

Chemicals, in addition to the refining process, are used to improve the mechanical properties (such as tensile strength), especially when the additional effects of refining are not desired. It is possible to distinguish between wet and dry strength, the latter being an inherent structural property mainly given by the development of fibre-to-fibre bonds [9]. Dry strength additives, such as starch and polyacrylamides, are water soluble and usually intended to behave as polyelectrolytes in cationic form, due to the introduction of ternary and quaternary amino groups. In this way, these additional components can act also as drainage and retention aids [9]. Some grades of paper (e.g., packaging, tea bag paper) require a high retention of strength in wet sheet, although generally the tensile strength of paper falls by around 90-97% when it becomes wet [9]. In this sense, wet strength agents are used to improve the sheet with the ability to retain a proportion of its dry strength when it becomes wet. Indeed, the tensile strength of wet paper is from 0-5% of the dry tensile strength without wet strength additives to as much as 15-50% with wet strength resins [31].

It is necessary that these agents are dispersible in water and reactive with fibres so that they can be retained during the sheet formation, often obtained by introducing cationic groups [9]. These additives that are thermosetting resins lead to the formation of covalent inter-fibre bonds [31]. The choice of a given wet strength agent depends on pH. In fact, urea- and melamine-formaldehyde resins are preferred to be used over an acidic pH range, while polyaminoamide-epichlorohydrin resins over a neutral or alkaline one [9].

1.2.2.3 Fillers

Pigments, usually referred to as fillers, are incorporated to the pulp for a number of beneficial effects [33]. They mainly improve optical properties, such as opacity and brightness of writing and printing papers, so that these paper grades represent by far the most dominant area for their application. Their presence reduces porosity, and generally the tendency of inks to migrate through the paper sheet. In addition, these additives can also have a buffering effect for paper acidity, reducing the cost of paper, being a cheap replacement for expensive fibres at 10-30% [31]. However, the filler content (loading) inevitably affects the properties of the paper. Higher levels of addition can cause a reduction in stiffness and strength given that fillers may interfere with inter-fibre bonding and alone are not able to impart strength [31].

Mineral fillers such calcium sulphate have been used since the 15th century in China, and have also been found in 18th-century Arabic paper. The first documented use of loading with china clay in Europe is dated back to 1807 [1]. There is also evidence of using calcium carbonate as a filler in Italian hand-made papers [34,35]. The beneficial effects of applying fillers in papermaking were already known in the 1871, when Rudolf Wagner stated that the moderate addition of a suitable mineral body to paper was by no means disadvantageous, and it was useful in several ways [33]. Nowadays, kaolin (also known as clay), calcium carbonate (also known as chalk or limestone), talc and titanium dioxide are mainly used as fillers [31]. In particular, precipitated calcium carbonate (PCC) followed by natural ground calcium carbonate (GCC) has become the most widely used fillers, applied within the body of the paper [33]. Table 1.4 reports typical filler loading levels in different European printing and writing papers.

Table 1.4. Filler loading (%) in printing and writing European papers, oven-dried. Adapted from [33].

Type of paper	**Filler and loading (%)**
Woodfree uncoated	20-27%
Copy, stationery, offset	PCC, GCC, chalk
Woodfree coating base	12-25%
Single, double, triple coated	Secondary, GCC, PCC, chalk
Wood-containing uncoated	30-37%
Supercalendered, magazine	Secondary, clay, GCC; PCC, talc
Newsprint	8-24%
Recycled/virgin fiber	Secondary, chalk, GCC

In a study [36] that involved analysis of 52 worldwide copy paper samples, it turned out that all papers had calcium carbonate-based fillers, except for one paper from India which contained talc. Particularly in woodfree uncoated paper, both internal, as described above, and surface filling, especially using GCC, can be applied. However, as it is well known, calcium carbonate is soluble under acidic conditions, so that its use requires neutral or slightly alkaline conditions. As a result of alkaline papermaking and calcium carbonate filler, an overall enhancement of paper durability is achieved. Moreover, given their role in replacing typical papermaking fibres, especially nowadays in the context of wood harvest and ever-growing competition due to biofuel, further investigations into how to increase the filler loading, maintaining stiffness and strength properties, are being carried out [33].

1.2.2.4 Brighteners

To improve the optical properties, in terms of whiteness and brightness, additives other than fillers can be applied in the papermaking processes, named fluorescent whitening agents (FWAs). Their diffusion in the papermaking practice established after the 1950s, although already known before [37]. FWAs enhance the reflection in the blue region of the visible light spectrum, absorbing UV radiation (around 300 nm) and emitting visible blue light (around 400 nm with a maximum reflectance at approximately 430 nm) due to fluorescence, while the long wavelength part remains nearly constant [37]. This behaviour is clearly visible comparing the reflectance spectra of paper with and without FWAs, as shown in Figure 1.13.

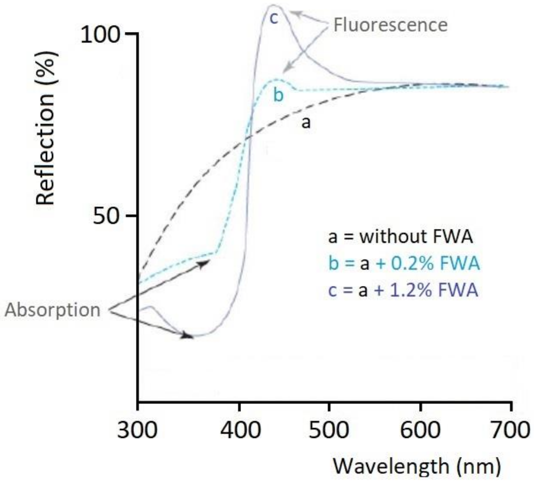

Figure 1.13. Reflectance spectra over 300-700 nm range of paper with and without fluorescent whitening agents (FWAs). Adapted from [37].

As far as the CIE L*a*b* colour coordinates are concerned [38], the effects of FWAs result in an increased L* value and a decreased b* value, thus enhancing the brightness and masking the inherent yellowness of the paper [37].

In paper industry, the derivatives of the 4,4′-diaminostilbene-2,2′-disulfonic acid are mostly used. Three different types of FWAs, according to the number of sulfo-groups, can be distinguished: disulfo, tetrasulfo and hexasulfo with two, four and six sulfo-groups, respectively. Given their operating mode, they can be effective with appropriate illuminant and amount of UV radiation. However, other factors related to their retention and interactions with fibrous and non-fibrous materials also influence their performance, the strongest influence coming from the pulp. Indeed, these agents perform best on bleached chemical pulps, not as good as on waste paper and unbleached pulps, as the lowest possible yellow tint of the raw materials ensures high gains in whiteness and brightness [37].

1.2.2.5 Other additives

In order to obtain paper with certain desired properties, some additives have to be retained, as mentioned above. In this sense, substances, classified as control additives, favour the retention of materials (e.g., fillers, internal sizing agents) in the final sheet [31]. The use of such additives in papermaking has been increasing over the last few decades, partially due to the increase use of fillers and recycled papers. These agents are water-soluble polymers which may be neutral or charged (cationic or anionic) [9]. The effects of retention are almost indistinguishable from that of drainage, so that they are usually considered together. In fact, any retention aid is able to improve the drainage rate of water from the pulp slurry [31].

Another type of additives, the so-called formation aids, promote the dispersion of the fibres. Traditionally locust bean gum, de-acetylated karaya gum, and guar gum have been reported to be effective dispersants for fibres [31].

1.3 Paper degradation

As paper materials are complex, their degradation is also complex. It involves many mechanisms that may act separately and/or influence each other. In general terms, ageing has been defined as the irreversible changes occurring slowly over time [39] which can eventually lead to such an extent of deterioration that paper becomes no longer usable. Degradation reactions can affect all paper components, fibrous and non-fibrous, in different ways. Independently of paper material complexity, the two main chemical mechanisms of paper degradation are hydrolysis and oxidation. Librarians and archivists should be now aware that degradation inevitably occurs, but it is accelerated by biological, physical and chemical factors. There are, in fact, a number of parameters that may influence the degradation rates and effects. It has been proposed to divide these parameters into two groups, namely endogenous and exogenous, as shown in Figure 1.14. The former group involves factors such as pH, metal ions and lignin, the latter one temperature, humidity, gaseous pollutants and light [5].

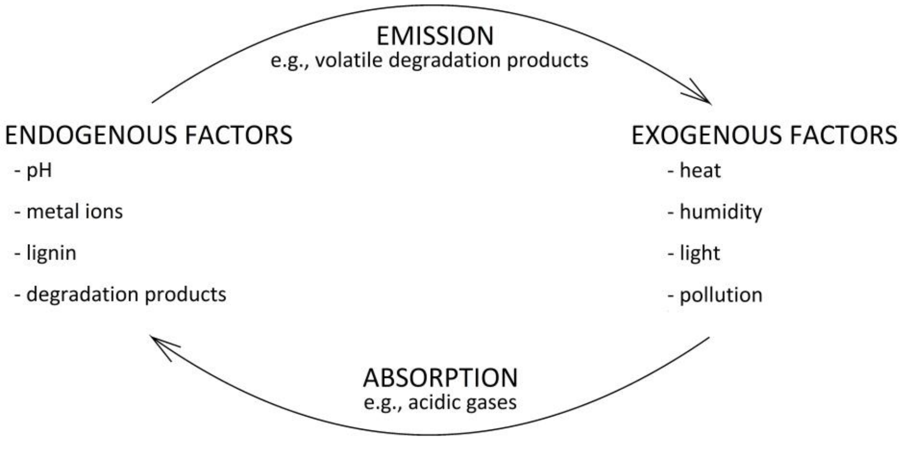

Figure 1.14. Factors affecting paper stability. Adapted from [5].

Temperature (T) and relative humidity (RH) conditions at which paper-based materials are stored play a crucial role in the longevity of paper, as well as, or maybe to a higher extent, the pH of the paper. Predictions of degradation rates of a historical Italian collection on the basis of the measured T, RH and pH values will be presented in Chapter 3.

Each factor can have different effects on paper degradation, when taken separately and/or in combination. As far as the acidity of paper is concerned, it is worth mentioning that gaseous pollutants such as SO_2, NO_x and O_3 are absorbed by paper, and their reaction with moisture may produce acids that catalyse the hydrolytic degradation. T is connected with the rate constants in an Arrhenius relationship, but at the same time, combinations of certain values of T and RH can provide suitable conditions for the development and growth of microorganisms, which in turn may cause further degradation. In fact, in addition to degradation due to physical and chemical factors, biological degradation can affect paper properties. Generally, hemicelluloses are more susceptible to biological attack than cellulose itself, while lignin can act as a protective agent. A number of biodeteriogens can contaminate paper substrate, different organisms and their related effects being associated with suitable environmental conditions (e.g., RH > 75% with T > 10°C) [40]. Such effects can alter chemical, mechanical and aesthetical properties. Microorganisms during their lifecycle produce enzymes which cause cleavage of macromolecules, and acid products which contribute to paper acidification. Evident mechanical damages can be provoked by insects (see Figure 3.8). Colour changes are frequently observed in paper contaminated by microorganisms (see Figure 3.7), as well as foxing damages [41]. Different strategies can be followed to contrast this type of degradation, by application of ethylene oxide gas or irradiation for fungi disinfection. An application of the latter method will be described in Chapter 4. Moreover, it is worth mentioning that another important factor involved in degradation processes is related to the anthropogenic actions, e.g., handling, bad practice of shelving.

1.3.1 Main reactions

It is possible to distinguish reactions affecting the cellulose chain in terms of the position at which they occur. In other words, reactions may take place at the bulk or at the ends of the chains. It is reasonable, as it will be discussed later, that the longer the chains are, better the paper stability is. Therefore, bulk-chain reactions are more harmful than the end-chain ones. As mentioned before, the two principal chemical reactions in degradation of paper-based materials are hydrolysis and oxidation, acid-catalysed hydrolysis being usually prevalent [42–44]. However, cellulose degradation should be regarded as a mixed oxidative and hydrolytic mechanism [45,46], in which the two reactions are autocatalytically accelerated by active oxygen species and protons, respectively. Transition metal ions can significantly contribute both to hydrolytic and oxidative reactions [47], as well as additives [48]. The nature and extent of physical and chemical changes depend on the specific reaction mechanism. Figure 1.15 shows a proposed summary of the main reactions occurring during natural ageing of cellulose [49].

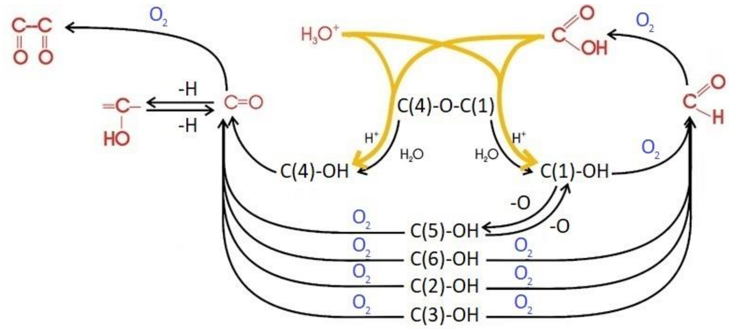

Figure 1.15. Reaction scheme for hydrolysis and oxidation of cellulose. Adapted from [49].

Generally, due to the key role of acidity in paper degradation, paper has been produced with alkaline reserve since the late years of the last century, and deacidification treatments have been performed on historical acidic collection for their preservation. Through deacidification, the hydrolytic process slows down, but some results [50] have demonstrated that caution has to be paid to possible side effects. For instance, the use of sodium tetraborate (borax) was found to cause appreciable changes in pH and alkaline reserve, but moist heat ageing involved a drastic decrease in DP ascribed to the presence of sodium ions [50]. For this reason, calcium-based salts are to be preferred [50].

1.3.1.1 Acid-catalysed hydrolysis

Hydrolysis takes place at the glycosidic bonds in presence of H^+ and water, the polymer chain splitting into two shorter units. It is a two-step reaction, as shown in Figure 1.16. Firstly, the addition of a proton occurs, then this is removed from the reaction product, acting thus as catalyst [51].

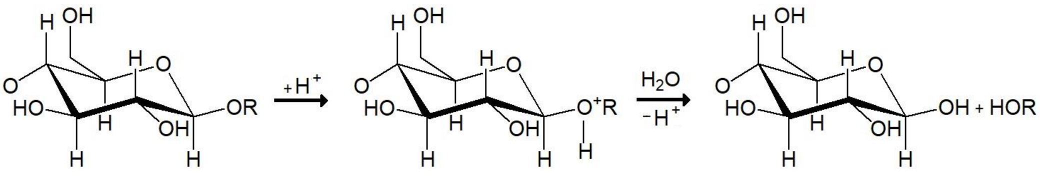

Figure 1.16. The two steps of acid-catalysed hydrolysis of cellulose. Adapted from [32].

As scissions of glycosidic bonds via hydrolysis is catalysed by acids, it is crucial that the pH of paper is neutral or alkaline to slow down the process. There can be several causes for paper acidity, use of aluminium sulphate with rosin being likely the primary one. This inevitably mounts concerns over the books and paper-based materials produced from the second half of the 19th century to the late 20th century, as it will be addressed in Chapter 3. In addition, oxidation of lignin or ink yields acidic products, as well as the formation of acids given by reactions between gaseous pollutants (such as SO_2, NO_x, O_3) with the water present in paper. On the contrary, alkaline reserves of Ca and Mg have a positive impact on paper stability.

Molecular mass distributions measured using size exclusion chromatography (SEC) suggested that hydrolysis occurs randomly along the polymer chain [43]. Additionally, as mentioned above, it should be considered that cellulose fibres are not homogenous, including crystalline and amorphous regions. In this regard, it is well known that the amorphous regions are more reactive than the crystalline ones, the degradation of crystalline domains appearing very slow, and with a small influence on the rate constant [52]. Moreover, it has been suggested that at the early stages of deterioration, chain scission occurs at random positions of the amorphous cellulose areas, while later the process becomes progressively less random [53]. The most sensitive part of cellulose is the amorphous domain, even because the reactants, for instance from polluted atmosphere, can enter the low-density region, being thus an access to chain for attack [44,49,53]. It has been also pointed out that in heterogenous media, such as cellulose, the influence of levelling-off DP (LODP, see below) [54,55], should not be neglected [56].

1.3.1.2 Oxidation

Due to the presence of hydroxyl groups along cellulose chains, they are sensitive to oxidation processes. The main reactions result in the formation of carbonyl and carboxyl groups at both the primary and secondary hydroxyl groups. These oxidised groups are chromophores, being thus responsible for colour changes, i.e. yellowing. Oxidation reactions can occur with possible consequent opening of rings or without, as shown in Figures 1.17 and 1.18, respectively, weakening the glycosidic bonds [45].

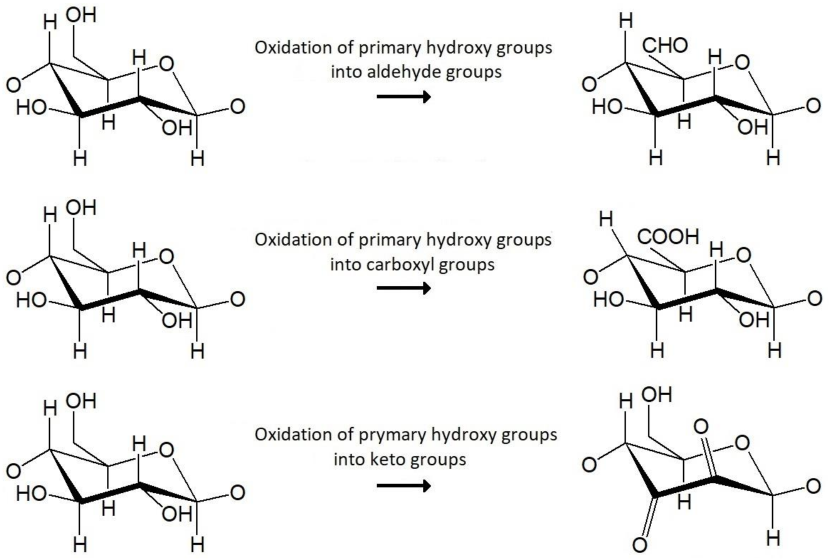

Figure 1.17. Main oxidation reactions without pyranose ring opening. Adapted from [45].

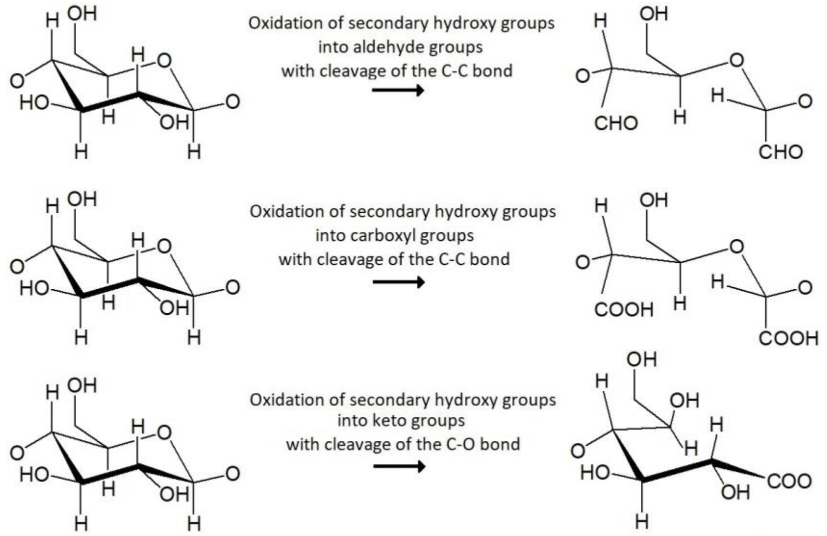

Figure 1.18. Main oxidation reactions with pyranose ring opening. Adapted from [45].

As highlighted by Zervos in his authoritative review [43], some authors [57,58] found that no detectable contribution in the degradation of pure cellulose derived from oxidative degradation, while other authors [59–63] have pointed out that this contribution should not be neglected, especially for neutral and alkaline papers. Oxidation may lead to the cleavage of glycosidic bonds, oxidised cellulose degrading faster than non-oxidised cellulose [45,48,57,64–66]. Moreover, the residues of the oxidised groups depend on the ageing conditions and paper composition. It has been shown, in fact, that paper containing lignin, hemicelluloses and additives is more prone to oxidation than paper of pure cellulose. These mechanisms can give rise to a wide array of possible degradation products depending on the oxidant and pH conditions.

The main cause of oxidative degradation is the presence of oxygen, although direct reaction between ground state oxygen and cellulose is forbidden by spin restrictions [48]. Oxidative processes play an important role during degradation of cellulose in alkaline environment, especially in the presence of transition metals, such as iron and copper [67]. Indeed, it has been shown that in neutral and alkaline conditions the role played by oxidation and alkaline degradation assumes major relevance. In alkaline conditions, three different pathways have been suggested: a radical chain, a ionic, and a mixed ion-radical chain mechanism, where the superoxide anion ($O_2^{\cdot -}$), the $HOO^{\cdot}$ and $HO^{\cdot}$ neutral radicals, and hydrogen peroxide (H_2O_2) are mainly involved [43,48].

The autoxidation that proceeds in an autocatalytic chain reaction involves free radicals, transition metal ions[10] also playing an important role, during thermal accelerated ageing. The latters, in fact, catalyse the production of free radicals from hydroperoxides. In this regard, the introduction of complexing agents can deactivate the transition metal by influencing its reduction/oxidative properties or by making it inaccessible to hydroperoxides [68].

It is worth noting, therefore, that oxidised cellulose chains that are not actually broken might be sites of further degradation, being easily degradable in both acidic and alkaline conditions. Indeed, if hydroxyl groups have been already oxidised to carbonyl and/or carboxyl functionals, it seems that the glycosidic bonds in their vicinity become weaker. Therefore, it turns out that cellulose degradation may be not only a consequence of acid-catalysed hydrolysis, but also of other possible degradation mechanisms, such as oxidation [32].

1.3.1.3 Other reactions

Whilst acids catalyse the scissions of the glycosidic bonds of cellulose chains, strong bases can initiate the alkaline degradation mechanism, that involves in sequence isomerisation, β-alcoxy elimination (also known as peeling reaction), tautomerization and benzilic acid rearrangement to glucoisosaccharinic acid [44,69]. By peeling reactions, single monosaccharide units are sequentially removed from the reducing end of the chain, both cellulose and hemicelluloses being affected. The reducing end of the polysaccharide isomerises to the ketonic form with consequent cleavage of the glycosidic linkage. The

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[10] Paper itself should contain metal content as low as not to present a problem, but amounts of metals (such as iron and copper) arose significantly in terms of degradation when certain inks are used [67].

product thus shortened by one glucose residue may undergo further degradation. As it is a sequential reaction, the DP of carbohydrates is reduced but not as severely as in a random process. The so-called stopping reaction, much slower than that of peeling, controls the extent to which the latter occurs [9]. As reported in the authoritative review by Area and Cheradame [44], these mechanisms become important in oxidised cellulose in an alkaline medium, e.g., after deacidification.

Furthermore, auto-crosslinking reactions can occur. They consist in the formation of hemiacetal bonds between carbonyls on neighbouring chains, produced by oxidation, or in the formation of ester linkages between carboxyl groups of a chain and hydroxyl groups of a neighbouring one. It is a competing mechanism as opposed to chain scission, an increase in tensile strength at the initial stage being attributed to cross-linking [43].

1.3.2 Measuring paper properties and degradation

In agreement with the complexity of paper and degradation mechanisms, a number of methods provide useful information on chemical and physical properties and their changes due to ageing. Physical and chemical changes are different depending on the prevalent reaction mechanism. For instance, a decrease of DP is a chemical evident effect due to hydrolytic degradation of cellulose, but at the same time it may cause a loss of strength, a physical change. An increase of carboxyl and carbonyl functionals is a chemical modification due to oxidation, but this also matches with changes of optical properties (i.e., yellowing). As mentioned above, additives, sizing, fillers are non-fibrous components useful to impart desired properties to paper. However, their presence can influence paper degradation and consequently it is important to be aware of their presence and amount also to elaborate appropriate conservation strategies. Over the time, even more methods have become available to characterise paper properties and ageing.

As already stressed, acidity plays a very important role in paper degradation. Therefore, it is reasonable that the most widespread chemical test in paper studies probably remains the determination of pH [70]. A number of methods have been proposed [71], and some standardised, to measure pH by cold extraction [71–73], or surface determination [74]. Surface measurements by means of pens containing mixtures of acid/base colour indicators were commonly used during collection survey since they do not require sampling, as reported in Chapter 3.

As far as destructive and/or invasive methods for paper characterisation are concerned, it is worth mentioning the test for fibre furnish analysis, namely, the determination of the fibrous components as regards the species and methods of pulping [75]. Other similar spot tests performed by applying appropriate reagents and observing colour reactions are also carried out to determine the presence of lignin [76] or non-fibrous components (e.g., animal glue [77], rosin [78]).

Another frequently used measurement, especially in connection to paper degradation, is the determination of DP or the average molecular weight. For this purpose, two main methods are usually employed, namely, viscometry and SEC, both of them requiring sampling and dissolution. Dissolution may be a source of complexity and systematic errors in the application of both methods for different reasons. For instance, the solvent commonly used, and suggested by many viscometric standards [79–82], is cupriethylendiamine (CED), which is not able to solubilise lignin, excluding thus paper made of mechanical pulp from such analyses. Moreover, another drawback that slightly complicates a very simple and little instrumentally demanding technique is that CED is fairly alkaline (pH=11). This leads to cellulose degradation, especially oxidised cellulose, by β-alkoxy elimination, due to exposure to atmospheric oxygen, so that some expedients are needed (such as CED and dissolved pulp solutions treated with nitrogen) to inhibit the process. There are other procedures for cellulose analysis by viscometry, such as that involving cadmium tri-ethylene diamine dihydroxide (also known as Cadoxen) which has a limited use, as no standard method is based on this dissolution, although it is less prone to oxidation [4]. Viscometric measurements lead to the calculation of the intrinsic viscosity $[\eta]$, a dimensionless value determined by limiting towards concentration zero the viscosity of cellulose solutions. As reported in the standard [79], after calibration of the viscometer, an appropriate mass of sample is defibrillated in a known volume of distilled water together with copper wires or stirrer bars. Once the paper sample has been completely disintegrated, CED is added with the same volume as water. The solution is shaken or stirred again until the sample is completely dissolved. The efflux time of this solution through a capillary viscometer, with suitable diameter, is recorded in a thermostated bath. This efflux time multiplied by a constant calculated by the calibration procedure leads to the calculation of the viscosity ratio, η_r. By comparing η_r with reference tabulated values and using Martin's equation [83], $[\eta]$ is determined. This value is then used in the Mark-Houwink-Sakurada equation (Eq. 1.1) which relates the intrinsic viscosity of a polymer to its viscosity-average molar mass (M_v) [84]:

$$[\eta] = K' \cdot M_v{}^a \qquad \text{(Eq. 1.1)}$$

where K' and a are constants for a given polymer-solvent system, temperature and molar mass range.

Many studies [85–89] have proposed different parameters to be used to calculate DP from $[\eta]$, most degradation studies having adopted those proposed by Evans and Wallis [88]. The viscometric method, therefore, provides information on M_v, and DP with a relatively simple procedure.

Changes in length of the macromolecules present in the paper matrix, due to acid- or alkaline-hydrolysis, are detected with a higher level of information by SEC, where the separation mechanism is based on difference in the hydrodynamic volume of solutes. SEC provides the molar mass distribution, on the basis of which it is possible to determine the number-average molar mass (M_n), and the weight-average molar mass (M_w), in addition to M_v that can be estimated if viscosity detectors are used. In order to carry out SEC, cellulose has to be dissolved. Cellulose derivatives can be more easily dissolved in conventional organic solvents, such as tetrahydrofuran. However, another option to dissolve cellulose involves the use of LiCl/N,N-dimethylacetamide (DMAc) [89–92].

Paper stability and degradation is also monitored through mechanical or physical paper properties, such as tensile strength [93], folding endurance [94], and tearing resistance [95]. Mechanical paper properties are associated with both length of macromolecular cellulose and intermolecular and interfibre bonding [9]. It has been shown that folding endurance is the most sensitive mechanical property for the detection of changes [96], being suggested as a suitable indicator of paper deterioration due to natural or accelerated ageing [58], although it may be affected by low repeatability [97]. Manual fold tests, where a page corner is folded back and forth as many times as it takes to break off on gentle pulling, were widely used during collection surveys [98,99]. Such manual fold tests and the standardised methods are all destructive techniques, and large samples are frequently needed due to a low repeatability of these measurements [70]. Numerous attempts have been performed to correlate mechanical properties with a more easily measurable quantity, such as DP [100–102]. Previous research has shown a correlation between tensile strength and folding endurance with DP [58]. On the basis of this correlation for which paper of very low DP corresponds to paper of low fold endurance and tensile strength, and due to the fact that such a paper is experienced by readers as brittle and difficult to handle, the occurrence of mechanical degradation has been recently associated with DP. However, wear and tear, as a form of mechanical degradation, were not found to accumulate as a function of DP when the latter is higher than 800 [103].

Among destructive tests implemented in paper characterisation and degradation studies, it is worth mentioning those carried out to determine carbonyl and carboxyl groups in order to monitor oxidation reactions. As it has been reported in Zervos' review, these methods recently changed going from the evaluation of the copper number[11] [104] to the application of chemiluminescence [105–110]. The latter technique started being used in polymer degradation research since Ashby showed that polymers emit weak light as they are heated [111]. It is presented as very advantageous, not being time-intensive, invasive, and destructive, in principle [106]. Carbonyl and carboxyl group profiles have been also investigated by combining group-selective fluorescence labeling with multi-detector gel permeation chromatography (GPC) analysis [112–115].

Another branch of the techniques frequently employed in the field of paper characterisation and degradation takes advantage of spectroscopy. These are increasingly becoming common, especially the non-destructive and non-invasive ones. Fourier-transform infrared (FTIR), Raman, UV-VIS reflectance spectroscopy, and nuclear magnetic resonance (NMR) are only a few methods that have been applied for studying paper documents [116,117]. Such methods in their suitable variants can allow studying foxing [118,119], changes due to ageing in terms of crystallinity [120], carbonyl and carboxyl groups [121,122], degradative products [47], as well as paper characterisation and identification of non-fibrous materials (such as fillers and sizing) [46,123]. In this regard, it is worth mentioning the recent development of a system based on near-infrared (NIR) spectroscopy in combination with chemometric data evaluation [124,125] to measure rapidly, non-destructively and non-invasively important chemical and physical properties, as it will be discussed in more detail in Chapter 3.

1.3.2.1 Accelerated degradation experiments

Chemical and physical changes normally (and hopefully) occur too slowly to be easily studied, experiments to speed up them being widely used in material science. In order

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[11] Amount of copper sulphate reduced by 100 g of pulp.

to study, or simulate, the physical and chemical reactions of paper degradation in a conveniently short time, accelerated ageing tests (also referred to as artificial ageing methods or degradation experiments) have been increasingly performed over the last decades. These tests mainly consist in exposing paper-based materials to extreme conditions of temperature and humidity, sometimes gaseous pollutants or particulate matter. Then, in order to be able to determine the ageing behaviour of a sample, the changes in some properties (e.g., DP) have to be followed over the time, so that the kinetics at those particular conditions can be evaluated. Several ageing procedures are standardised [126–129]. The conditions at which the degradation experiments can be performed vary significantly. For instance, this variability concerns T and RH at which the tests are conducted (e.g., 80°C and 65% RH), constant or cycling conditions, paper exposed as loose sheet or stack, in closed vessels or microclimatic chamber, inclusion of other degradation agents (e.g., iron gall inks, microorganisms), with or without light. The T range is usually between room T and 105°C. It has been suggested that at higher temperatures the mechanism of degradation can be different from those occurring at ambient conditions [130]. Moreover, at $T > 100°C$ the control of RH becomes difficult. On the contrary, no lower T limit has been suggested, provided it is suitable to allow a short duration ageing [43]. The exigency to fix humidity in addition to temperature came out to mimic natural ageing [60,131]. Later, it was concluded that a 30-80% RH range covers the variations occurring in natural ageing conditions, although RH values out of this range are also used. It has been also recognised that the importance of humidity in paper degradation experiments is not directly associated with RH, but with the moisture content (MC) of paper [132], which in turn is a function of T and RH. Zou et al. [132] have explicitly suggested to consider MC rather than RH in degradation experiments. A linear dependence of MC on RH is probably a good approximation only in a limited range of RH values [133]. Recent studies, which involved degradation experiments or their applications [134,135], have evaluated MC according to the equation reported by Paltakari and Karlsson [136]. As far as the present thesis work is concerned, the water vapour pressure (P_v) instead of RH is considered as the variable parameter in the degradation experiments, as it will be discussed in Chapter 2, with the aim to determine separately the effects of T and P_v. As known, equal RH values at different temperatures are associated with different P_v values.

Given the huge variability of the conditions at which degradation experiments can be performed, it had better outline their main achievable goals, that are predictions of degradation rates, comparison of stability between different paper samples, and studies of degradation mechanisms [70]. The results of such experiments can provide useful evidence also for the applicability of conservation treatments [50]. These tests have been extensively carried out although their applicability was a matter of controversy from several points of view. The reliability of using high temperature without undesired side reactions was discussed by several authors [39,42,137,138]. It has been questioned whether accelerated tests, conceived for studying the stability of modern paper, provide reliable results also for paper which have already undergone natural, and potentially different, processes of natural ageing. Accelerated ageing could in principle involve chemical reactions not typical of natural ageing. In other words, it has been questioned whether such methods involving elevated temperature can simulate the rate of natural degradation, and thus whether the Arrhenius equation is applicable to the study of change of certain mechanical and chemical properties of cellulose. An authoritative review by Porck [42] provides an overview of the state of art concerning possibilities and limitations of such experiments and addresses the questions mentioned above. Although this review is not so recent, it is very useful to have a critical perspective on this topic. The main conclusion drawn is that only qualitative aspects of natural ageing can be reliably predicted by means of accelerated ageing tests, their application being encouraged in studies of paper conservation treatments. Nevertheless, such experiments are recently widely used, and a dose-response function, modelled on the results of some of these experiments, has been recently proposed in order to predict degradation rates of historical paper as a function of T, RH, and pH [134].

1.3.3 Kinetics of acid-hydrolytic degradation

Kinetic studies of paper degradation are mainly aimed at determining rate laws (and possibly the corresponding mechanisms of reaction), rate constants and activation energies. These aspects are generally investigated by measuring the DP of cellulose or other properties as a function of time [43,132,139].

Early studies of cellulose degradation from a theoretical statistical point of view should be dated back to the work of Kuhn and co-authors in 1930 [140,141]. The early model for the degradation of linear polymers was introduced by Ekenstam in 1936 who proposed for cellulose degradation a first order reaction with respect to glycosidic bonds [142]. It is well known that, considering the concentration ([A]) of a generic compound over time (t), a first order kinetics leads to the following differential form (Eq. 1.2) [143]:

$$-\frac{d[A]}{dt} = k\,[A] \qquad \text{(Eq. 1.2)}$$

where k is the rate constant, expressed in t^{-1}. Integration of Eq. 1.2 gives the following equation:

$$\ln\frac{[A]}{[A]_0} = -\,k\,t \qquad \text{(Eq. 1.3)}$$

In the case of cellulose materials, where linear homopolymers are subjected to random degradation and cellulose chains have different chain lengths, [A] can be replaced by the total number of unbroken inter-monomer glycosidic bonds (L) in a given volume, obtaining Eq. 1.4:

$$\ln\frac{L_t}{L_0} = -\,k\,t \qquad \text{(Eq. 1.4)}$$

where L_0 and L_t are the number of unbroken inter-monomer glycosidic bonds at time 0 and t, respectively.

L_0 and L_t can be defined in terms of number of monomers (N), and number of chains (M), as in the following equations (Eq. 1.5 and Eq. 1.6):

$$L_0 = N - M_0 \qquad \text{(Eq. 1.5)}$$

$$L_t = N - M_t \qquad \text{(Eq. 1.6)}$$

where M_0 and M_t are the number of chains at time 0 and t, respectively, and N is supposed to be constant as the degradation reaction occurs.

The average DP is defined as the ratio between the number of monomers and number of chains (Eq. 1.7):

$$DP = \frac{N}{M} \qquad \text{(Eq. 1.7)}$$

Therefore, DP at time 0 and t can be rewritten as in Eq. 1.8 and Eq. 1.9, respectively:

$$DP_0 = \frac{N}{M_0} \qquad \text{(Eq. 1.8)}$$

$$DP_t = \frac{N}{M_t} \qquad \text{(Eq. 1.9)}$$

Expressing M as a function of DP, Eq. 1.5 and Eq. 1.6 become:

$$L_0 = N - \left(\frac{1}{DP_0}\right)N = N\left(1 - \frac{1}{DP_0}\right) \qquad \text{(Eq. 1.10)}$$

$$L_t = N - \left(\frac{1}{DP_t}\right)N = N\left(1 - \frac{1}{DP_t}\right) \qquad \text{(Eq. 1.11)}$$

Therefore, introducing Eq. 1.10 and 1.11 in Eq. 1.4, it turns out:

$$\ln\frac{N\left(1-\frac{1}{DP_t}\right)}{N\left(1-\frac{1}{DP_0}\right)} = -kt \qquad \text{(Eq. 1.12)}$$

As the number of monomers N is constant, it can be eliminated. Then, Eq. 1.13 is obtained:

$$\ln\left(1-\frac{1}{DP_t}\right)-\ln\left(1-\frac{1}{DP_0}\right)=-kt \qquad \text{(Eq. 1.13)}$$

By applying the virial series, i.e. $-\ln(1-x)\cong x$, which can be used if $\frac{1}{DP}\ll 1$, whereby $DP \gg 1$, Eq. 1.14 is finally obtained:

$$\frac{1}{DP}-\frac{1}{DP_0}=kt \qquad \text{(Eq. 1.14)}$$

which describes a second-order rate law with respect to DP [143].

The Ekenstam equation (Eq. 1.14) can thus be applied under the following assumptions: the hydrolytic cleavage is the main mechanism, the polymer chain has a high average molecular weight (i.e., $DP \gg 1$), there is no loss of monomers.

As far as the kinetic models are concerned, Zou and co-authors in a remarkable study [132] have demonstrated that without any assumption about the uniformity of the reaction and its order (e.g., first, second), the rate of DP change during the period t and $t+\Delta t$ is obtained by the following equation (Eq. 1.15):

$$\frac{dDP_t(t)}{dt}=\lim_{t\to 0}\frac{DP_t(t+\Delta t)-DP_t(t)}{\Delta t}=-k(t)DP^2 \qquad \text{(Eq. 1.15)}$$

Integration of Eq. 1.15, a typical second order kinetics [143], yields:

$$\frac{1}{DP}-\frac{1}{DP_0}=\int_0^t k(t)dt \qquad \text{(Eq. 1.16)}$$

Where $k(t)$ is a rate constant which can vary with time, when the above requirements are not satisfied. When the rate of bond cleavage is constant, the classical kinetic equation (Eq. 1.14) is obtained.

The same rate law in terms of DP (Eq. 1.14) can also be derived assuming a constant bond scission rate (zero-order reaction rate) [144].

Different stages and rates of degradation were observed experimentally. Degradation in heterogeneous cellulose may occur in several stages [43]. In a first rapid stage, rarely reported because a very limited number of bonds are involved, weak links, due to mechanical stresses [145,146] or oxidised groups [45,57,147], are hydrolysed [148]. Then, the degradation of cellulose proceeds with random hydrolysis of the glycosidic bonds in the amorphous domain, following Eq. 1.14 [43]. A slower state follows, where the crystalline regions are attacked, the applicability of classical kinetic equation being no longer valid. This deceleration starts as DP reaches the LODP value, which is assumed to be the asymptotic DP value of degradation, namely the average chain length in the crystalline regions [43,56], which depends on the nature of the cellulose sample. For further details upon the kinetics and mechanisms of paper degradation, the reader can be referred to [43,52,56,66,149]. Finally, it can be useful to summarise that the kinetic of paper degradation for random acid-hydrolytic reactions is mainly described as a first-order kinetics with respect to the number of unbroken glycosidic bonds, L, which leads to the Ekenstam equation (Eq. 1.14). The rate constants are thus obtained by the slopes of linear plots where the reciprocal of DP is reported as a function of time.

The degradation rate constants are related to the temperature according to the well-known Arrhenius equation:

$$k = Ae^{-\left(E_a/RT\right)} \qquad \text{(Eq. 1.17)}$$

where A is the frequency factor, with the same dimensions as k (t^{-1}), E_a is the activation energy ($J\,mol^{-1}$), R is the gas constant ($J\,mol^{-1}K^{-1}$) and T is the absolute temperature (K). Degradation of paper in neutral or alkaline medium mainly derived from two contributions (i.e., hydrolysis and oxidation). The measured E_a can thus result from the activation energies of different processes. The observed E_a and A values are obtained plotting $\ln(k)$ values vs the inverse of the corresponding T values. The validity of Arrhenius equation for cellulose materials has been demonstrated in the temperature range 60-220 °C [70]. Using the Arrhenius equation, it is possible to evaluate the rate constant for degradation at room temperature, a very important parameter for practical purposes. Although such applications of Arrhenius equation have been a matter of controversy in the literature (concerning for instance the considerable uncertainty due to extreme values of T in the degradation experiments) [42,70], the temperature of the storage areas in libraries, archives and museums is anyway suggested to be as low as possible in order to slow down the deterioration processes. Some standards suggest temperatures under 20°C [150–152], while more recently different temperature ranges have been proposed (e.g., 13 – 23 °C [153,154]). Critically, it should be considered that, although Arrhenius relationship suggests temperatures as low as possible, practical problems arise at lower temperatures. For instance, provided it were possible, storing books at 5 °C would require particular caution to handle them because of their fragility at that temperature, and would arise issues related to the surrounding RH levels, which at such a low T could cause condensation, determining high mould risks.

The pre-exponential factor A is a function of parameters which influence the paper degradation. As mentioned before, significant differences have been found between dry-heat and moist-heat ageing [58,131,155]. It has been suggested [132] that A can be mainly expresses as a function of acidity and moisture content:

$$\mathrm{A = f\,([H_2O], [H^+], \dots)} \qquad \text{(Eq. 1.18)}$$

where $\mathrm{[H_2O]}$ and $\mathrm{[H^+]}$ are the concentrations of water (i.e., MC) and hydrogen ions adsorbed in the paper. In other words, the number of broken bonds per unit time, that is proportional to the rate constant, depends mainly on T, pH and MC. In this regard, with reference to conservation strategy and practice, another application of the Arrhenius equation can be found in a recent dose-response function modelled for historic papers [134]. This function, discussed in more detail in Chapter 3, considers the rate constant as a function of thermo-hygrometric (T and RH) and paper (pH) conditions:

$$\mathrm{k = f\,(T, RH, pH)} \qquad \text{(Eq. 1.19)}$$

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CHAPTER 2

RECYCLED AND NON-RECYCLED CONTEMPORARY PAPER: CHARACTERISATION AND KINETICS OF DEGRADATION

Abstract

This Chapter presents a study aimed at investigating the kinetics of degradation of two types of contemporary paper, recycled and non-recycled. To provide a context for this study, a brief outline of the main steps of papermaking is given, pointing out that recycling generally affects fibre and pulp properties.

The two types of paper were characterised in terms of acidity, dry matter, ash content, lignin presence, and fibre furnish. Degradation experiments were carried out at different temperatures (50-80 °C) and water vapour pressures (90.5-227.5 torr). Other analyses, i.e. viscometry and colorimetry, were performed to evaluate the effects of degradation. In particular, DP was measured as a function of time to describe the rate laws and calculate rate constants and activation energies.

Colour changes were found to be perceptible to the human eye in samples aged for more than 40 days at 60, 70 and 80 °C. As expected, the degradation rates were found to follow the rate law found by Ekenstam, that is, a linear correlation between $1/\mathrm{DP}$ and t. The rate constants measured for the recycled paper were found to be slightly higher than those of the non-recycled paper, although comparable within experimental limits.

Interestingly, the measured kinetic constants do not increase monotonically with increasing water vapour pressure, a maximum being found at intermediate levels. The activation energies, supplied by the Arrhenius dependence of the rate constants on temperature, fall in the typical range expected for paper degradation. Finally, the measured rate constants fit fairly well a dose-response function recently modelled for historic papers.

2.1 Introduction

Paper as writing material can be made of different fibrous sources (e.g., hardwood, softwood and paper for recycling), a growing part of the paper manufacturing process involving currently recycled fibres. While in the past wood fibre sources were used to manage the ever-increasing demand for paper and deficiency of rag fibres, as underlined in Chapter 1, nowadays economic and environmental pressures encourage the use of recycled paper. Actually, the use of recycled paper in the papermaking was pioneered by Matthias Koops in 1800 with one of his patents[12] [1], and started being of industrial relevance since 1826, when Koops established the Neckinger mill, which produced white paper from printed waste paper [2].

Recycled fibres play an increasingly important role for global paper industry as a substitute for virgin fiber pulps [3]. The annual reports published by the Confederation of European Paper Industries (CEPI)[13] reveal how fast the recycling rate grew almost steadily from the early 1990s to the beginning of 2000s, from about 40% in 1991 to approximately 62% in 2005. Even though recycling rates are levelling out in the last years, reaching 72.3% in 2017 after having achieved 72.0% the year before [4], a new target of 74% recycling rate is intended to be reached by 2020 [5]. It is worth specifying that the recycling rate is defined by CEPI as the ratio between recycling of used paper, including net trade of paper for recycling, and paper and board consumption [6].

Generally, in order to have fibres of whatever nature (wood, non-wood or recycled) suitable to produce paper, these fibres should be in such a form so that they result more susceptible to changes; for instance, bonds should be easily formed between fibres when wet suspensions are dried. In a review by Hubbe and co-authors [7] this process is referred to as ‘activation’, where pulping can be considered as the first step. This word and its antonym (i.e., ‘deactivation’) sound particularly useful in the context of recycling. Indeed, it has been reported that agents that enhance bonding during papermaking can make fibres less prone to reform strong inter-fibre bonds during recycling [8,9]. For instance, additives, such as cationic starches, are introduced into pulps with the intention to be retained on cellulosic materials. A significant proportion of such additives can remain attached to fibres

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[12] «…for a mode of extracting printing and writing ink from printed and written paper, and converting the paper from which the ink is extracted into pulp, and making thereof paper fit for writing, printing, and other purpose» A.D. 1800 – N. 2392 [1].

[13] http://www.cepi.org/topics/statistics?date%5Bvalue%5D%5Byear%5D=2018&field_type_value=All

also when they are recycled. In addition to pulping processes, which can be mainly mechanical, semi-chemical or chemical, as mentioned in Chapter 1, another process involved in the fibre preparation is the so-called refining, whereby fibres are subjected to compression and shearing forces [10]. Increased refining is another example of those factors which improve fibre bonding during papermaking, but reduce their capability to form bonds when recovered paper is converted into recycled paper. Pressing is another process which influences fibre properties, especially their water-holding capacity [7]. As briefly outlined above, numerous processes are involved in papermaking and recycling, and additional processes (e.g., coating, bleaching) can be necessary when a particular paper grade is desired. For further information the reader can be referred to [7,11–13].

Of course, before using paper for recycling to produce recycled paper, it is necessary to recovery it. Paper recycling, in fact, mainly consists in collection and recovery of paper for recycling, repulping, and deinking, in addition to the papermaking processes applied to virgin fibres (e.g., drying, bleaching). The techniques involved in all the steps of recycling, from recovery to deinking, are continually evolving. Over the last years, important advances in pulping, flotation deinking and cleaning/screening led to significant improvements in the quality of paper made from secondary fibres [12]. As far as the initial step is concerned, different grades of paper can be recovered, which will find different uses in paper production. It is possible to clearly distinguish between pre- and post-consumer recovered paper, where the former comprises material from manufacturing, waste from papermaking process and finished paper from obsolete inventories, while the latter includes paper, board and fibrous materials recovered from stores, collected from households, offices, schools, etc. The complete process to be applied to recovered paper is given by its grade and the specific requirements of the final paper product [12]. For instance, while mixed-grade papers are primarily used for the production of packaging papers and boards, for graphic paper production deinked grades are mainly used [3]. In this regard, it is to be noted that there are tests to evaluate recyclability and deinkability [14,15]. Then, once paper for recycling has been collected and recovered, different steps are involved in paper production, mainly aimed at removing contaminants [16]. A series of processes can be used to accomplish this task, recycling can be thus defined as a combination of various treatments carried out to produce pulp from recovered papers and to clean it to produce new paper [12]. There are also many possible ways of arranging these steps [16]. However, mechanical dispersion of paper into its component fibres in water, namely repulping, is needed, as mentioned above. Despite the high shear and energy involved, this process seems to provoke little damage to individual fibres as a result of the initial repulping [7]. A series of cleaning operations, which can be physical or chemical, follow in order to remove non-fibrous components (e.g., metal, elastic, adhesives, ink particles). Paper for recycling is usually already printed upon, therefore one of the most important process involved in the production of high quality grades is the removal of ink. It is worth mentioning that the intuition of the practice that is currently named deinking is attributed to Justus Claproth, a jurist who published a booklet entitled "An invention to make new papers from printed papers by washing out the printing ink completely from the pulp" in 1774. Deinking is a process whereby ink particles are removed through washing and/or flotation [3], after having adjusted the fibre suspension increasing its pH [17]. Indeed, two main steps are followed for deinking. The first one consists in ink detachment from the surface of fibre suspension, the second one involves ink removal by washing or flotation. Ink detachment is usually performed through stirring and chemical action of additives which contribute to the disintegration of the recovered paper, alkaline agents being more efficient than neutral agents. For instance, sodium hydroxide assists in swelling of the fibres which favours loosening print particles, thus allowing the release of the ink pigment [17]. Depending on various factors such as the particle sizes of ink and paper grades to be produced, washing can be sufficient, combination with flotation being used for more efficient deinking. Globally, the use of deinked paper in newsprint dominates, followed by hygienic papers and printing and writing papers [12].

The quality of paper made from recycled fibres is generally considered to be worse than that of virgin material, but the behaviour of different types of pulp can vary considerably [17]. As outlined in Chapter 1, there are various parameters that can influence mechanical and chemical properties of paper and, consequently, its ageing behaviour. It is reasonable that the quality of paper made from recycled fibres is related with the quality of paper for recycling and the processes involved in recycling and papermaking, to the same extent as paper resulted from rag or wood fibres through acidic or alkaline processes. In other words, recycled pulp quality is affected by the history of the fibres, processes and treatments that these fibres have experienced. In this regard, fibre history has been subdivided into five periods: fibre furnish and pulping; papermaking process; printing and converting; consumption and collection; recycling process [18]. Therefore, the processes involved in paper recycling can have different effects on the properties of the resulted recycled paper, different characteristics between virgin (i.e., non-recycled) and recycled fibres being detectable [18].

Numerous studies have shown a reduction mainly in physical strength properties of recycled fibres in comparison to those of virgin fibres [7,17,19,20], and the source of this has been related to basic fibre features, such as strength, length, swelling, and bonding potential [19–21], although attempts to trace the cause of these effects are still not resolved [12]. In this regard, it is worth noting that chemical pulps show a higher reduction in strength on recycling than mechanical pulps, and biggest effects occur the first time that delignified pulp is dried and recycled [17]. As mentioned in Chapter 1, chemical and mechanical pulps are chemically and physically different, recycling effects on these pulps being also different. However, most of these changes can be ascribed to drying, a process that inevitably causes a partially irreversible closure of small pores in the wall of fibres, further modifications being attributed to the effects of degradation of ageing and contaminants [7,12]. Physical changes that take place in papermaking fibres upon drying [22] or, in other words, changes that occur on water loss in cellulose are usually described with the term "hornification" [14], although there is not an unanimous definition of this word [7]. It has been reported that hornification of recycled fibres is a stiffening effect on the cell wall, as a result of drying in papermaking [23]. When chemical fibres undergo repeated drying and rewetting, they are hornified and can significantly lose their originally high bonding potential [21,23–28]. On the contrary, originally weaker mechanical pulps improve somewhat during a corresponding treatment, several studies having shown a good recyclability of such fibres [29,30]. The water retention value is a measure of the degree of hornification [28]. Indeed, the irreversible pore closure leads to a reduction in water content of cell wall, causing a loss in fibre flexibility and less effective inter-fibre bonding, although no reduction in strength of the fibres themselves has been detected [17]. To a certain extent, this accounts for an increased tear resistance, stiffness and air permeability of paper during recycling [17,28]. Effects of hornification depend not only on the chemical nature of the pulp, but also on its physical state and amount of lignin. It has been shown that unbeaten pulps show an increase in tensile strength during drying/rewetting [18,28,31], and bleached pulps exhibit a greater extent of hornification [24,28]. Although the main effects of recycling processes have been related to alterations of mechanical properties of paper, other changes can occur influencing chemical and optical properties. As far as the latter properties are concerned, brightness slightly decreases [28], while paper opacity increases

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[14] The introduction of this word in the field of papermaking is attributed to G. Jayme in 1944, originally translated into English as "cornification", then changed to "hornification" [22].

during the whole recycling process, higher values being observed at high drying temperatures (e.g., 120 °C) [2,17]. Moreover, it has been reported that changes of macromolecular weight distribution, polydispersity, and degree of polymerisation due to pulp recycling are not linear throughout the recycling process. A decrease of DP was generally observed and attributed to glycosidic bond cleavages, cellulose cross-linking accounting for a moderate increase in some stages of recycling [32].

Thanks to the improvement of recycling technologies in recent years, the quality of paper made from secondary fibres is approaching that of virgin paper [12]. However, because of the alterations which occur during the overall recycling process, the recycled pulps may receive additional treatments and chemicals to produce the desired grade of paper, which may include mechanical or chemical procedures and blending with virgin fibres [2]. Recycled office paper is currently available on the market with a share of recycled fibres ranging between 50 and 100%.

2.2 Aim of the study

Recycling has been proved to affect to different extents several properties of the resulted paper. In addition, while mechanisms and rates of degradation have been extensively studied for historic paper, providing very useful tools for characterisation and preventive conservation of historical paper-based collections, less studies have focused on contemporary paper, and even less on recycled paper, whose production has been significantly increased over the last years. In this context, the present study, already published [33], was carried out to investigate the kinetics of degradation of recycled and non-recycled contemporary papers.

2.3 Materials and Methods

2.3.1 Paper types

Two types of contemporary paper, recycled and non-recycled, were analysed, both manufactured by Fedrigoni S.p.A. (Verona, Italy):

- Arcoprint 1 EW (A_{NR}) composed by ECF cellulose [34];
- Woodstock (W_R) composed by 20% ECF cellulose, and 80% pre-consumer recycled fibres [35].

As far as bleaching is concerned, it is worth mentioning that ECF bleaching, based on chlorine dioxide, has become the industry standard [36].

2.3.2 Methods for paper characterisation and evaluation of degradation effects

Non-degraded samples of both types of paper were characterised in terms of their fibre composition, lignin presence, acidity, ash and dry matter contents, DP, and colour. The two latter properties were measured also on degraded samples at different ageing times in order to evaluate the effects of degradation as a function of time. All the techniques employed[15] are destructive and/or invasive, except colorimetry.

2.3.2.1 Fibre furnish

Staining analytical methods are commonly used in fibre identification because they are simple, rapid and not expensive although they may include subjective errors and low accuracy [37]. In this study, the standard procedure ISO 9184-1 [38] was followed. This method is applicable to all kinds of pulps and most papers and boards, including those containing more than one kind of fibres and different pulping processes, but it is not suitable for papers heavily impregnated or highly coloured, as the former can be scarcely dispersed and the latter can affect the staining reactions of the fibres. It is to be noted that this method was here employed on a representative quantity of stained fibres of both types of paper samples, only at a qualitative level, namely, looking at the stain reactions and morphological characteristics of the fibres. As suggested by the standard procedure for ordinary samples, torn test pieces were inserted into a test tube, where deionised water was added and the suspension heated on a hot-plate up to boiling, stirring occasionally. Although the dispersion of the fibres for both samples required a while, no additives (such as sodium hydroxide) was added. As suggested by the standard procedure ISO 9184-2 [39], which assists in choosing the appropriate staining test for the performance of fibre furnish analysis, given that the aim of such analysis in the present study was to evaluate the kind

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[15] Fibre furnish analysis, phloroglucinol test, and cold extraction were carried out at the Institute for Sustainable Heritage of the University College of London during a 6-month visiting research period, with the supervision of Prof. Matija Strlič. Colour measurements were performed at the Conservation Science Laboratory for Cultural Heritage of the University of Bologna. Ash and dry matter content determinations were carried out by Prof. Irena Kralj Cigić (Faculty of Chemistry and Chemical Technology, University of Ljubljana).

of pulp (e.g., chemical or rag pulp) and identify some morphological features of the fibres, the Herzberg reagent was employed. Therefore, the standard procedure ISO 9184-3 [40] was followed to stain fibres and examine them under the microscope. Fresh Herzberg stain was prepared. Therefore, from the dilute fibre suspension, by means of a Pasteur pipette, a sufficient quantity was transferred onto a clean microscope slide. To further separate fibres and facilitate their identification, the fibres were dispersed using a dissecting needle. Then, the slide was dried on the hot-plate, 2-3 drops of the reagent were applied, as shown in Figure 2.1. A cover glass was then put on avoiding formation of air bubbles, and the potential excess of stain was removed.

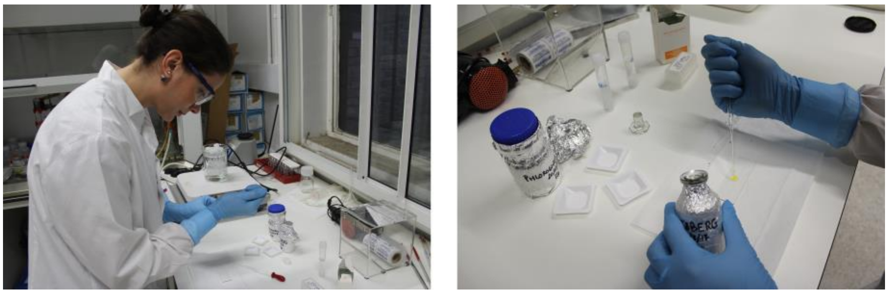

Figure 2.1. Preparation of microslides for fibre furnish analysis. Left: withdrawals of fibre suspensions from the test tubes on the hot-plate. Right: addition of Herzberg reagent.

Because of the instability of certain stains, the analysis was performed as soon as the slide was prepared. To test the prepared Herzberg reagent, analysis on pure cellulose paper (Whatman No.1, Maidstone) as the standard reference was carried out, staining wine-red as expected. At least two slides for each sample of paper were prepared and evaluated using a digital microscope (Keyence-VHX 5000) with polarised light, and an optical microscope (Brunel Microscope, SP400), equipped with a camera (Canon EOS 1100D), as shown in Figure 2.2. Using the digital microscope, images were acquired also in high resolution in order to better identify morphological characteristics for fibre identification.

Figure 2.2. Observation of microslides for fibre furnish analysis. Left: using a digital microscope. Right: using an optical microscope.

2.3.2.2 Lignin presence

The lignin presence was determined by the phloroglucinol spot test, carried out following the procedure described by the standard TAPPI T401 [41]. Fresh phloroglucinol reagent, prepared and stored in the dark, produces a magenta colour in contact with groundwood, partly cooked unbleached chemical pulp, and some other sources of ligneous fibres. It is to be noted that this measurement is not quantitative, it only provides an approximate evaluation of the presence of lignin. The phloroglucinol test was carried out on paper samples and on the fibre suspensions, prepared as for fibre furnish analysis. To test the phloroglucinol reagent, lignin free paper (Whatman No.1, Maidstone) was used as reference standard and no colour change was observed.

2.3.2.3 Acidity

Acidity can be estimated in several ways, as mentioned in Chapter 1, extraction methods being the most common. Strlič and co-authors [42] have compared several methods and showed that most extraction methods give comparable results for acidic samples, except for samples surface-sized with gelatine. In addition, they pointed out that to measure the pH of alkaline aqueous extracts, the effects of atmospheric carbon dioxide and slow dissolution of earth-alkali metal carbonates have to be considered. Indeed, the combination of the two latter factors has been estimated to account for a difference of more than 1.5 pH units. For this reason, here it was adopted a method proposed by Strlič and co-authors [42], specifically suitable for pH determinations of alkaline paper, based on equilibration with carbon dioxide and dissolution of carbonates. The mean uncertainty for pH measurement of alkaline paper is evaluated to be $\pm$ 0.3 [42].

For both types of paper, the determination of pH was carried out using a micro-combined glass electrode (Mettler Toledo, InLab® Micro 51343160). Five determinations for each sample were performed. The samples were weighted (2.86 ± 0.03 mg) and put into 1.5 mL vials. 200 μL MilliQ water were added and the vials were shaken frequently. The pH values reported were obtained until a constant pH reading was reached. All the pH values were rounded to the nearest 0.1 decimal digit.

2.3.2.4 Ash and water content

Residue on ignition (ash) and moisture content were measured following the standard procedures ISO 2144 [43] and ISO 638 [44], respectively. For both measurements, about 200 mg of sample for each type of paper was weighted after drying at 105 °C for 3 h, and after maintaining at 900 °C for 1 h, to determine the moisture content and the residue on ignition, respectively. Three determinations for each sample were performed. Ash and water contents measured were taken into account when calculating the mass of paper samples for evaluation of DP values.

2.3.2.5 Viscometry

Determination of DP by viscometric measurements is the most widely used method to evaluate the extent of degradation, and as outlined in Chapter 1, the standard procedure ISO 5351 [45] specifies a method which yields the limiting viscosity number $[\eta]$ of a pulp in a dilute CED solution. In brief, an appropriate mass of sample was defibrillated in a known volume of water and then the same volume of 1.0 M CED solution was added, so that eventually the sample was completely dissolved in 0.5 M CED solution. Limiting its exposure to air, the efflux time of the solution, thermostated in a water bath at 25.0 ± 0.1 °C, was measured by means of a capillary-tube viscometer (Ubbelohde, 532 10 I), as shown in Figure 2.3.

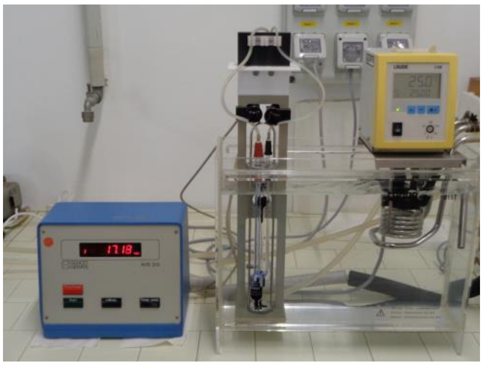

Figure 2.3. Experimental set-up for viscometric measurements.

The capillary-tube viscometer for the measurements and the concentration of each sample were set in order to satisfy the requirements of the standard. The product between a constant, obtained through the viscometer calibration procedure, and each measured efflux time of the solution yielded the η_r (dimensionless). $[\eta]$ was determined by comparing η_r with the reference tabulated values of $[\eta] \cdot \rho$, where ρ is the mass concentration (g mL^{-1}), calculated considering the ash and moisture contents of paper samples. Finally, DP values were calculated by means of the Mark-Houwink-Sakurada equation (Eq.1.1) [46], with the set of parameters proposed by Evans and Wallis [47]:

$$\mathrm{DP}^{0.85} = 1.1[\eta] \qquad \text{(Eq. 2.1)}$$

Each DP value was obtained from two samples and two measurements of efflux time were carried out for each sample. As mentioned above, viscometry was carried out not only on the non-degraded samples, but also on the degraded ones at each withdrawal during the ageing experiments. The uncertainty of DP determinations was evaluated to be about ±3%.

2.3.2.6 Colorimetry

For colour measurements a portable spectrometer (Minolta, CM-2600d), equipped with an internal integrating sphere of 56-mm diameter in reflectance geometry d/8 and three Xenon pulsed lamps, was used operating in the specular component excluded mode. A white plate (Minolta, CM-A145) was employed for calibration. Reflectance spectra were acquired in the 360-740 nm range, with a resolution of 10 nm, and a 3-mm diameter aperture, using the D65/10° measurement conditions [48]. Five spectra were measured on five different points of each samples. The data were processed using the SpectraMagic^{TM} NX (Version 2.7) and Microsoft Excel software to calculate the average CIELAB coordinates for each sample. The CIELAB colour space is produced by plotting along three perpendicular axes the L^*, a^* and b^* coordinates [49] that, in simple terms, represent lightness, red-green and yellow-blue colours [50], respectively, as shown in Figure 2.4.

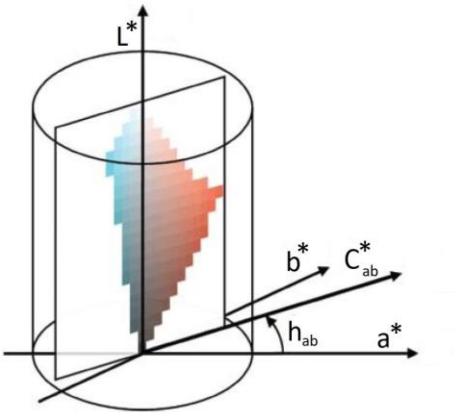

Figure 2.4. Representation of a perspective view of cylindrical coordinates in CIELAB space. Adapted from [50], where C_{ab} and h_{ab} are the CIELAB chroma and hue angle.*

Colorimetry, as well as viscometry, was applied to both the non-degraded and degraded samples, the effects of degradation in terms of colour change being thus investigated. Colour differences in the CIELAB space can be calculated in several ways. In this study, colour differences (ΔE), were calculated according to two different formulas, $\Delta E^*{}_{ab}$ and ΔE_{00}. Indeed, one of the most widely used methods to evaluate colour changes is the CIE 1976 colour-difference formula, denoted with $\Delta E^*{}_{ab}$, that is the Euclidean distance of two points in the CIELAB space, as reported in Eq. 2.2:

$$\Delta E^{*}_{ab} = \sqrt{(\Delta L^{*})^2 + (\Delta a^{*})^2 + (\Delta b^{*})^2} \qquad \text{(Eq. 2.2)}$$

where ΔL^{*}, Δa^{*}, and Δb^{*} are the differences between L^{*}, a^{*}, and b^{*} values of two analysed samples [51].

The colour changes were also estimated using the more recent CIEDE 2000 colour-difference formula, denoted with ΔE_{00}, reported in Eq. 2.3:

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T\left(\frac{\Delta C'}{k_C S_C}\right)\left(\frac{\Delta H'}{k_H S_H}\right)} \qquad \text{(Eq. 2.3)}$$

This formula, far more sophisticated than the simple Euclidean distance, is defined on new coordinates which are written as function of the known coordinates (L^{*}, a^{*}, b^{*}) of the CIELAB system. The reader can be referred to [49–52] for further details. In this study, the Microsoft Excel implementation available online [53], described by [54], was used to calculate ΔE_{00}.

2.3.3 Accelerated degradation experiments

Accelerated degradation experiments are more and more often being used to investigate paper degradation effects and mechanisms, as discussed in Chapter 1. It is worth briefly summarising that such experiments consist in exposing a material to extreme conditions of temperature, humidity and/or other degrading factors (such as gaseous pollutants and particulate matter) in order to accelerate natural degradation processes and, thus, investigate the changes occurring in the material as a function of time and experimental conditions. The possibilities and limitations of these tests were reviewed by Porck [55]. Degradation experiments are usually carried out in climate chambers or in closed vessels, although the results obtained with the two methods can differ [56,57]. In this regard, a standard procedure [58] has been devised, based on the claim that accelerated ageing in airtight vials better simulates the natural ageing process because it allows the interaction of paper with its degradation products [59]. Some studies have provided evidence that the ageing process of pure cellulose paper in sealed vessels is indeed autocatalytic, and new kinetic models have been proposed [60–62]. In contrast, other kinetic studies of accelerated ageing in both closed and open systems, as monitored by DP and breaking length measurements, have shown that no statistically meaningful difference of the degradation rate can be observed, although, at the same time, the interaction of paper degradation products with the paper itself has been confirmed, based on pH and whiteness index values [63].

In the present study, degradation experiments were carried out in closed desiccators placed into an oven[16], as shown in Figure 2.5. The desired conditions of temperature and humidity were achieved using glycerine-water solutions at different concentrations depending on the conditions to be achieved [64]. Saturated salt solutions (e.g., NaCl) have been used in ageing tests, but salt deposits on the strips of paper samples, which may affect their degradation, were observed [65]. To the best of our knowledge, glycerine-water solutions have never been used in paper degradation experiments. In addition, such solutions allow achieving different humidity levels by simply changing the concentration, while different salts are needed for changing humidity [66]. Therefore, solutions at different concentrations, measured by refractive index, were prepared for each desired thermo-hygrometric condition, and placed at the bottom of the desiccator, as shown in Figure 2.5.

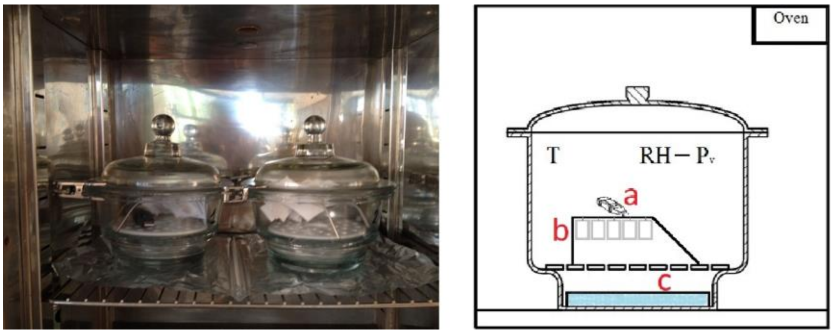

Figure 2.5. Ageing experiments. Left: desiccators during ageing experiments. Right: reproduction of the experimental set-up, where the red letters indicate (a) datalogger sensor, (b) paper samples, and (c) glycerine-water solution.

Moreover, as far as humidity, one of the most important agents of deterioration, is concerned, it is to be highlighted that this parameter is generally accounted for in terms of its content relative to a given temperature, i.e., RH (%). In contrast, in the present research water vapour pressure (P_v), instead of RH, was directly considered as a variable parameter, with the aim of determining separately the effects of T and P_v. For this reason, two kinds of degradation experiments, the first keeping constant T and changing P_v, the second *vice versa* keeping constant P_v and changing T, were carried out, as reported in Table 2.1.

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[16] Degradation experiments were carried out at the laboratories of the Department of Chemistry, and at the Inter-Departmental Research Centre for Environmental Science – CIRSA of the University of Bologna. However, further degradation experiments, not reported in this thesis, conducted in collaboration with the University College of London and University of Ljubljana, are being carried out using a larger variety of recycled and non-recycled samples (i.e., 8 types of office paper) in climate chambers at two different ageing conditions.

Table 2.1. Thermo-hygrometric conditions (T, P_v and RH) for the degradation experiments performed with Arcoprint (A_{NR}) and Woodstock (W_R) paper [33].

Paper sample	**T (°C)**	**P_v (torr)**	**RH (%)**
A_{NR}	70	90.5	39
		99.8	43
		146.3	63
		190.4	82
		227.5	98
A_{NR}	50	90.5	98
W_R			
A_{NR}	60		61
W_R			
A_{NR}	70		39
W_R			
A_{NR}	80		26
W_R			

The ageing tests were carried out over a period ranging from 40 to 55 days, samples being degraded in one desiccator for each combination of T and P_v, with quick sample withdrawals every 5–6 days. Thermo-hygrometric dataloggers, placed into the desiccators in order to measure T and RH throughout the experiments, showed that the desired conditions were restored within 2 h after each opening.

2.4 Results and Discussion

In this section, the results of the analyses performed are discussed separating those carried out on the non-degraded samples (for paper characterisation) from those carried out on the degraded samples (for evaluation of degradation effects and rates, with an emphasis on the latter aspect).

2.4.1 Paper characterisation

The two non-degraded papers were found to be essentially equal in terms of alkalinity, ash and water contents, but somewhat different for the initial DP values (DP_0), considering the experimental errors of each measurement, as reported in Table 2.2.

Table 2.2. pH, ash and water content, along with DP_0 values with their standard deviations of unaged Arcoprint (A_{NR}) and Woodstock (W_R) papers [33].

	A_{NR}	**W_R**
pH	8.5±0.2	8.6±0.1
ash content (%)	12.0±0.2	12.1±0.2
Water content (%)	3.6±0.2	3.5±0.1
DP_0	2330±60	1890±50

As far as the fibre furnish is concerned, the bluish-violet colour of the fibres upon addition of the Herzberg stain [40], as shown in Figure 2.6, indicated that both papers are made of chemical pulp.

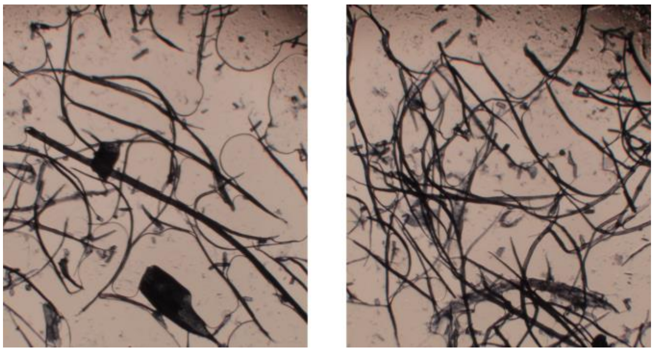

Figure 2.6. Optical micrographs, where the bluish-violet colour indicates that both papers are made of chemical pulp. Left: Arcoprint. Right: Woodstock.

Moreover, further analysis of the microslides by digital microscopy allowed to identify more clearly and with a higher resolution features of hardwood and softwood fibres (i.e., vessels and pinoids, respectively) in both types of paper, as shown in Figure 2.7.

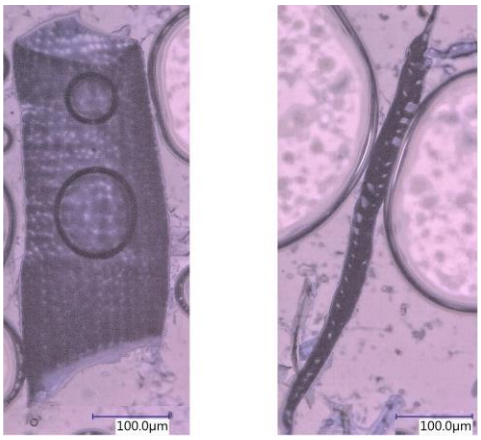

Figure 2.7. Digital micrographs, where identification features of wood fibres are visible. Left: hardwood fibre. Right: softwood fibre. Adapted from [33].

Another common feature between the two types of paper is the presence of lignin. As shown in Figure 2.8, both papers, especially the recycled one, turned slightly magenta with addition of phloroglucinol reagent, in comparison with the reference Whatman lignin free paper.

Figure 2.8. Optical micrographs of paper sample upon addition of phloroglucinol. Left: Arcoprint. Centre: Woodstock. Right: Whatman No.1.

Lignin presence is an important factor not only because of its involvement in degradation mechanisms, but also for the viability of the viscometric method [45], so that viscometry should not be used for lignin contents > 4%. Although the analyses performed using the phloroglucinol reagent do not provide quantitative results, the colour reactions indicated that a sufficiently small content of lignin was present in both types of paper. This is also supported by the fact that small lignin contents are expected for the present delignified pulps.

2.4.2 Paper degradation

The results of colorimetry and viscometry carried out on the degraded samples at the ageing conditions reported in Table 2.1 are discussed to evaluate the degradation effects.

2.4.2.1 Colour changes

It is well known that colour changes may occur during degradation [67–71]. Spectroscopic and chemical studies have provided evidence that yellowing is ascribed to the formation of carbonyl groups [68,69,71], the reduction of the HOMO/LUMO energy gap causing the consequent absorption in the visible range.

The visible reflectance spectra of the non-degraded and degraded samples of both types of paper are shown in Figure 2.9.

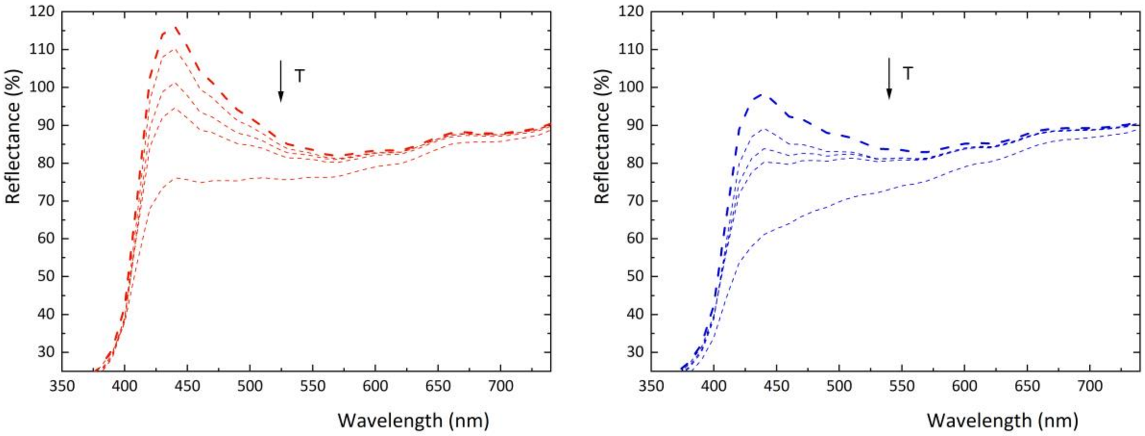

Figure 2.9. Visible reflectance spectra at constant P_v (90.5 torr) in which the top thicker curve is relative to the non-degraded samples, the lower curves represent the spectra of the most degraded samples at T=50, 60, 70 and 80 °C. Left (red): Arcoprint. Right (blue): Woodstock. Adapted from [33].

At first sight, the spectra of the degraded samples exhibit an evident intensity reduction of the peak around 450 nm (blue region) which increases with increasing temperature, as expected. In addition, the spectra of the non-degraded samples, and in particular for the peak around 450 nm, resemble the typical spectra of paper that contains fluorescent whitening agents (see Figure 1.13), suggesting that both papers, especially Arcoprint, may contain these additives.

In this study, colour changes were also evaluated in terms of the CIELAB colour coordinates, and colour-differences (i.e., ΔE^*_{ab} and ΔE_{00}). Table 2.3 reports the colour coordinates L^*, a^* and b^* of the non-degraded and most degraded samples at constant P_v (90.5 torr) and four different T for both types of paper.

Table 2.3. Colour coordinates with their standard deviations of the non-degraded and most degraded samples at constant P_v (90.5 torr) and four different T (50, 60, 70 and 80 °C) for Arcoprint (A_{NR}) and Woodstock (W_R) paper[33].

	L^*	**a^***	**b^***
A_{NR} (unaged)	94.41 ± 0.03	3.05 ± 0.04	-13.08 ± 0.12
W_R (unaged)	93.96 ± 0.06	1.87 ± 0.04	-5.29 ± 0.12
A_{NR} (T=50°C)	93.86 ± 0.04	2.67 ± 0.07	-10.87 ± 0.19
W_R (T=50°C)	92.81 ± 0.10	1.62 ± 0.03	-1.65 ± 0.17
A_{NR} (T=60°C)	93.35 ± 0.10	1.95 ± 0.11	-7.22 ± 0.34
W_R (T=60°C)	92.70 ± 0.07	0.92 ± 0.09	0.94 ± 0.31
A_{NR} (T=70°C)	92.77 ± 0.11	1.57 ± 0.17	-4.66 ± 0.50
W_R (T=70°C)	92.40 ± 0.06	0.66 ± 0.05	2.44 ± 0.22
A_{NR} (T=80°C)	90.29 ± 0.02	1.27 ± 0.09	2.44 ± 0.32
W_R (T=80°C)	88.95 ± 0.08	1.11 ± 0.05	10.38 ± 0.23

Figures 2.10, 2.11 and 2.12 show the trend of L^*, a^* and b^*, respectively, with the ageing conditions.

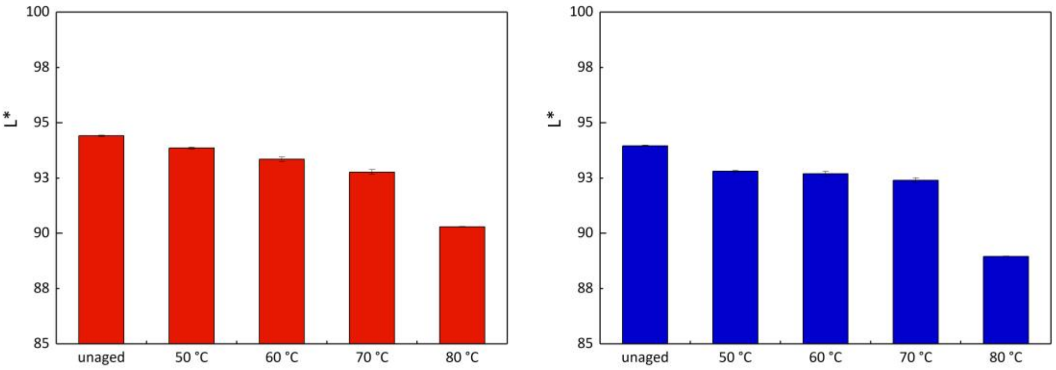

Figure 2.10. L^* component trend. Left (red): Arcoprint. Right (blue): Woodstock.

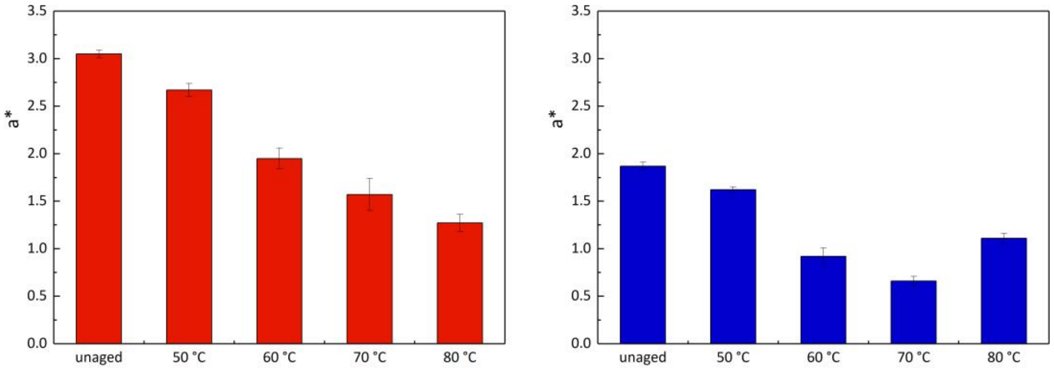

Figure 2.11. a^* component trend. Left (red): Arcoprint. Right (blue): Woodstock.

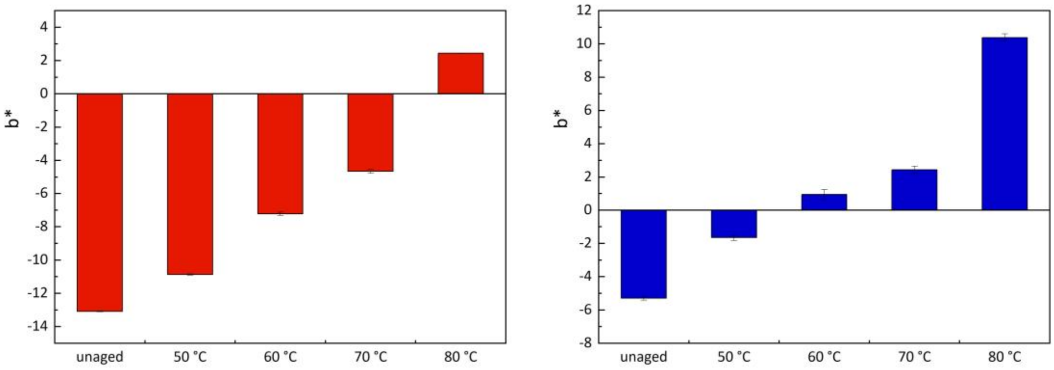

Figure 2.12. b^* component trend. Left (red): Arcoprint. Right (blue): Woodstock.

It is evident that the L^* component, indicating the lightness, gradually decreases, as expected, with increasing temperature, as well as the a^* component does mostly. On the contrary, the b^* component, which accounts for the yellowness, increases significantly with increasing temperature, the considerable change in this component being consistent with oxidation processes and/or degradation of optical brighteners.

As far as the colour differences is concerned, Table 2.4 reports ΔE^*_{ab} and ΔE_{00} values calculated as described in the previous section.

Table 2.4. Colour differences express as ΔE^*_{ab} and ΔE_{00} calculated relative to non-degraded samples for Arcoprint (A_{NR}) and Woodstock (W_R)[33].

	ΔE^*_{ab}	ΔE_{00}
A_{NR} (T=50°C)	2.31	1.51
W_R (T=50°C)	3.83	3.26
A_{NR} (T=60°C)	6.06	4.17
W_R (T=60°C)	6.43	5.75
A_{NR} (T=70°C)	8.70	6.23
W_R (T=70°C)	7.98	7.28
A_{NR} (T=80°C)	16.16	12.72
W_R (T=80°C)	16.47	13.92

ΔE^*_{ab} has been widely used over to last decades, although it is going to be replaced by ΔE_{00} . However, regardless of the formula used, the interpretation of ΔE is not straightforward. As far as ΔE^*_{ab} is concerned, it has been reported that the so-called Just Noticeable Difference (JND) is equal to 2.3 [72], other authors indicating $\Delta E^*_{ab} = 4$ as a colour variation appreciated by human eye [73], while according to Hardeberg [74] perceptual impact of ΔE^*_{ab} is as follows: < 3 hardly perceptible; 3-6 perceptible but acceptable; > 6 not acceptable. The concept and value of a perceptible colour change is also debated in terms of ΔE_{00}. $\Delta E_{00} = 1.5$ has been suggested as the threshold value for visible perception of colour variation through experiments carried out at the Victoria & Albert Museum [75]. In light of these considerations, the calculated ΔE values provide evidence for perceptible colour changes for both papers degraded at T = 60, 70, and 80 °C, degradation at T = 50 °C causing ΔE^*_{ab} and ΔE_{00} values above the onset of perceptibility only in the recycled Woodstock paper.

2.4.2.2 Kinetics of degradation

Several kinetics models have been proposed to describe cellulose degradation, as discussed in Chapter 1. However, the kinetic of cellulose degradation is commonly accepted to follow a first-order rate law with respect to the number of unbroken glycosidic bonds (see Eq. 1.4) [76–79], which can be re-formulated in terms of DP through the Ekenstam equation (Eq. 1.14):

$$\frac{1}{\mathrm{DP}} - \frac{1}{\mathrm{DP_0}} = \mathrm{kt}$$

where DP and $\mathrm{DP_0}$ represent the degree of polymerisation of cellulose at time t and 0, respectively, and k is the rate constant.

As reported in Table 2.1, in the present study two sets of degradation experiments were carried out keeping constant and changing T or P_v, alternatively. Figure 2.13 and Figure 2.14, respectively, display the plots of the reciprocal DP versus t for Arcoprint paper degraded at constant T (70 °C) and four different P_v, and for both types of paper aged at constant P_v and four different T.

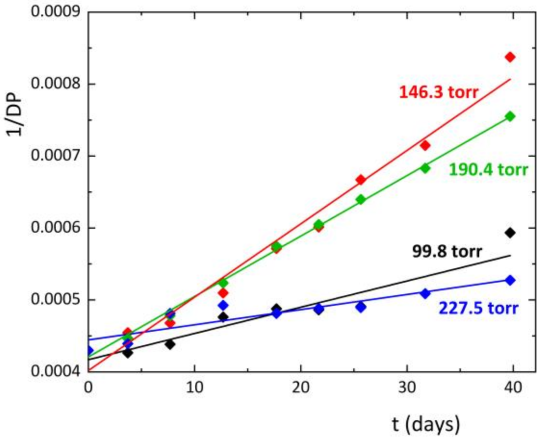

Figure 2.13. Reciprocal DP as a function of time for the degradation experiment using Arcoprint at constant T (70 °C) and four different P_v. Adapted from [33].

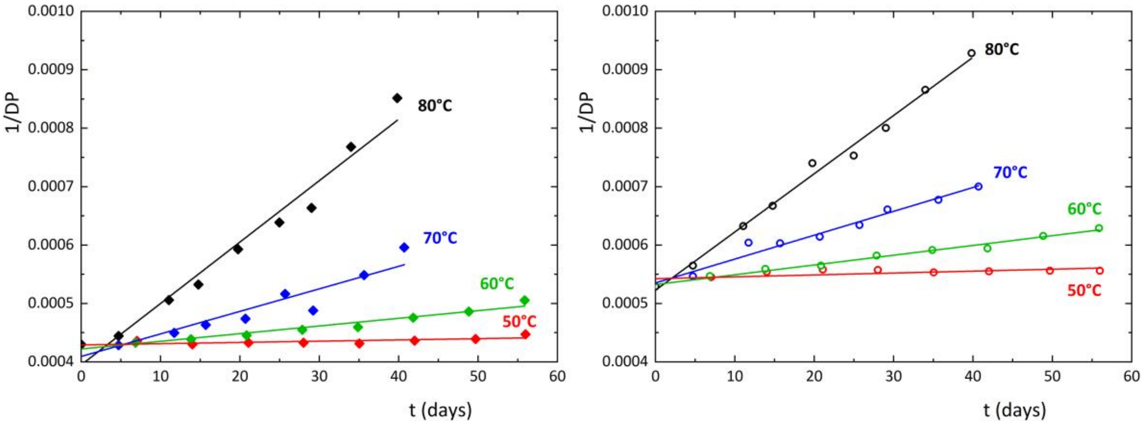

Figure 2.14. Reciprocal DP as a function of time for the degradation experiments using Arcoprint (left) and Woodstock (right) at constant P_v (90.5 torr) and four different T. Adapted from [33].

As expected in accordance with Eq. 1.14, Figures 2.13 and 2.14 show good linearity of the plots, whose slopes lead to the calculation of the rate constants reported in Table 2.5 by linear regression for each ageing experiments.

Table 2.5. Rate constants calculated for each ageing condition with the corresponding uncertainties and correlation coefficients (R^2) [33].

Paper sample	T (°C)	P_v (torr)	RH (%)	k · 10^6 (day^{-1})	R^2
ANR	70	90.5	39	3.856 ± 0.517	0.89
		99.8	43	3.644 ± 0.506	0.88
		146.3	63	10.199 ± 0.581	0.98
		190.4	82	8.405 ± 0.157	0.998
		227.5	98	2.105 ± 0.372	0.82
ANR	50	90.5	98	0.214 ± 0.072	0.56
WR				0.325 ± 0.134	0.46
ANR	60		61	1.311 ± 0.115	0.95
WR				1.673 ± 0.079	0.98
ANR	70		39	3.856 ± 0.517	0.89
WR				4.083 ± 0.254	0.97
ANR	80		26	10.511 ± 0.708	0.97
WR				9.97 ± 0.325	0.99

The order of magnitude (10^{-6} · day^{-1}) found for the rate constants is in line with the literature [78,80], taking the effects of other parameters (such as pH, T and RH) into account. The rate constants measured for both the non-recycled and recycled paper were found to be comparable, considering the associated uncertainties, although the rate constants of the recycled paper were generally found to be somewhat higher than the corresponding constants of the non-recycled paper.

As far as the trend of the slopes is concerned, it is worth noting that they increase monotonically with T, as expected, unlike what happens with P_v. Interestingly, the rate constants measured at constant T (70 °C) do not increase monotonotonically P_v (see Figure 2.15). The trend displays a maximum at intermediate levels of P_v, considering that the 90.5-227.5 torr P_v range corresponds to a 39-98 % RH range at 70 °C (see Table 2.5.).

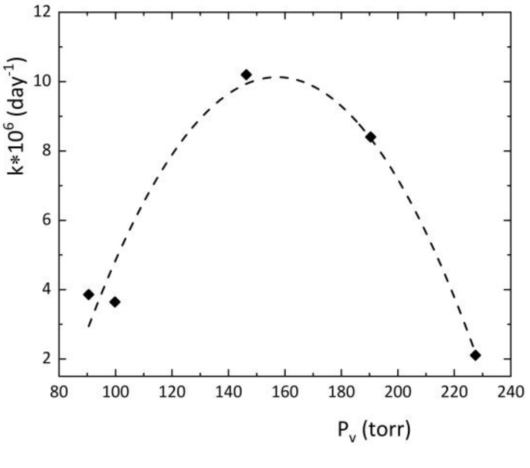

Figure 2.15. Rate constants as a function of P_v found for the ageing experiments carried out using Arcoprint at constant T (70 °C). Adapted from [33].

It has been reported that degradation rates of acidic paper increase with increasing RH [78]. However, other authors [81] have concluded that the rates of degradation of neutral and alkaline pulps in either dry or highly humid conditions are slower than those occurring at intermediate levels of RH, the fastest rate being found in the 60-80 % RH range. The decreasing partial pressure of oxygen with increasing water pressure in the atmosphere, along with the saturation of paper with water, which reduces oxygen diffusion, account for the rate decrease at high water pressures [81]. The results of the present study, where a maximum rate was observed around 70 % RH, are consistent with the latter study taking into account the alkalinity of the paper analysed (see Table 2.2).

Moreover, as outlined in Chapter 1, the degradation rate follows an Arrhenius dependence on T, $\ln(k)$ being linearly related to $1/T$ (see Eq. 1.17). Figure 2.16 displays the Arrhenius plots of both types of paper degraded at constant P_v.

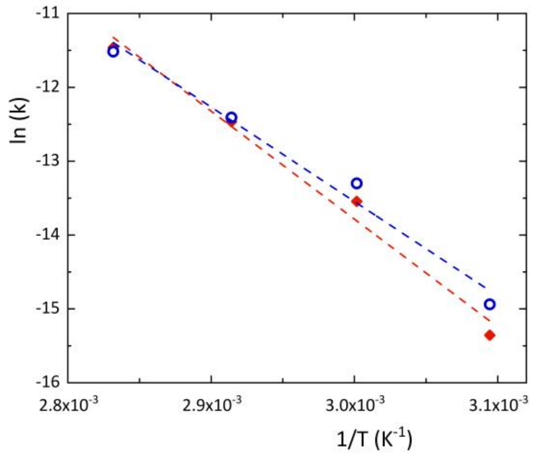

Figure 2.16. Arrhenius plots of the rate constants of Arcoprint (red) and Woodstock (blue) at constant P_v (90.5 torr). Adapted from [33].

A good $\ln(k)$ versus $1/T$ linearity can be observed for both types of paper. The activation energies (E_a) calculated as the slopes of each curve by linear regression are reported in Table 2.6.

Table 2.6. Activation energies E_a calculated for both types of paper, Arcoprint (A_{NR}) and Woodstock (W_R), with the corresponding uncertainties [33].

Paper sample	$\mathbf{E_a}$ **($\mathbf{kJ\ mol^{-1}}$)**	$\mathbf{R^2}$
A_{NR}	121.5 ± 10.8	0.98
W_R	106.3 ± 10.5	0.98

The E_a values found are in line with those typically reported for hydrolytic degradation of cellulose, i.e. 104-133 kJ mol^{-1} [78,80,82]. However, it is worth mentioning that there is a considerable variation in the activation energies for degradation of cellulosic materials depending on the conditions of degradation, ranging from 27 to 165 kJ mol^{-1} [83,84]. The E_a found for the recycled paper is somewhat smaller than that found for the non-recycled one, although they result to be comparable considering their uncertainties.

Moreover, it is to be noted that while so far the analogous Arrhenius plots reported in the literature were obtained at constant RH, the experiments in the present study were carried out at constant P_v. In the present experiments RH ranges widely from 26 % (T = 50 °C) to 98 % (T = 80°C). Correspondingly, the moisture content, as evaluated by Strlič and co-authors [80] and originally reported by Paltakari and Karlsson [85] varies from 1.7 to 12.4 %. According to Zou and co-authors [78] the moisture content significantly affects the pre-exponential factor of the kinetic constant.

Finally, the rate constants found in the present study were compared with those included in the modelling of a dose-response function, recently published [80], which describes the dependence of the degradation rate constants on environmental factors and material properties (i.e., pH). This function has been modelled by taking into account various types of paper with different compositions and manufacturing technologies, recycled paper being not included, and it allows predicting rate constants as a function of T and RH of the environment and pH of the paper, being thus a useful tool for preventive conservation of historical collections, as reported in Chapter 3. Figure 2.17 displays the scatterplot reported by Strlič and co-authors [80] with the addition of the results of the present study.

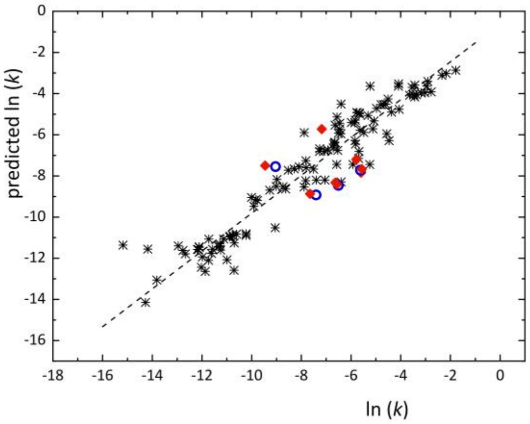

Figure 2.17. $ln(k)$ *(year*$^{-1}$*) values measured in this study and those predicted by the dose-response function [80]. The red and blue symbols are associated with Arcoprint and Woodstock paper, respectively. Adapted from [33].*

It is to be noted that with respect to the previously reported data, on the basis of which the curve has been modelled, nine of the new points lie below the curve, the remaining three being above. This indicates that the measured rate constants that correspond to the points below the curve are 4-5 times larger than the corresponding values predicted by the dose-response function. On the contrary, the degradation rates corresponding to the points above the curve are lower than those predicted by the function. In this regard, as pointed out above and displayed in Figure 2.15, the latter points are relative to the degradation experiments performed at the highest RH level (i.e., 98 %), for which rate constants were found to be lower than those obtained at intermediate RH levels. However, generally, it can be concluded that the new points added lie quite close to the previously reported data. Figure 2.18 shows the linear regression line with 99% prediction bands, elaborated on the previously reported data [80] using OriginPro 2017 (Origin Lab Corporation). All new points are distributed in the 99 % prediction bands.

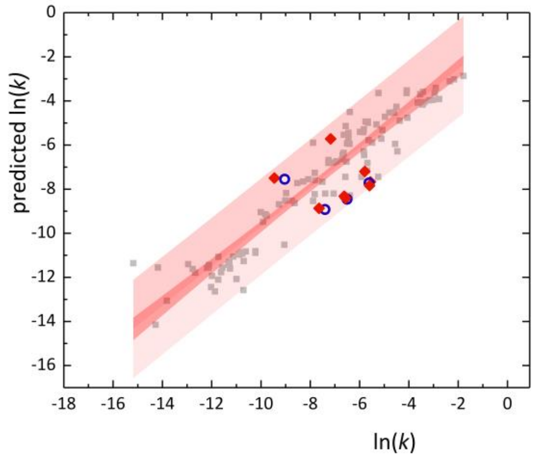

Figure 2.18. Comparison between $ln(k)$ *(year*$^{-1}$*) values measured in this study and the linear regression line with 99% prediction bands.*

2.5 Conclusions

Two types of contemporary paper, one recycled and the other one non-recycled, were used to investigate their degradation behaviour through accelerated ageing experiments. The non-degraded papers were characterised, and resulted to be made of chemical pulp, with both softwood and hardwood fibres, and possess a comparable alkaline pH, ash and water contents, but a different DP.

By performing accelerated degradation experiments at various T and P_v, these papers were degraded to evaluate the colour changes, using the ΔE^*_{ab} and ΔE_{00} parameters, and kinetics of degradation, looking at the decrease of DP as a function of time. About the former aspect, colour changes were found to be appreciable to the human eye (i.e., ΔE^*_{ab} > 3 and ΔE_{00} > 1.5) for both the recycled and non-recycled paper degraded at 60 °C or higher temperatures. As far as the kinetics of degradation are concerned, the rate constants were found from the slopes of the linear plots $1/DP$ vs t. The rate constants calculated for the recycled paper, although somewhat higher, were found to be comparable with those of the non-recycled paper considering the experimental limits.

The Arrhenius relationship allowed the calculation of the activation energies, which fall in the typical range reported in the literature. The activation energies found for the recycled and non-recycled paper were found to be comparable within experimental limits, although that of the former resulted to be slightly smaller.

It is worth stressing that the trend of the rate constants as a function of P_v was not found to be monotonic, unlike the results previously reported in the literature for acidic paper. Higher rate constants were found at intermediate levels of RH (i.e., about 70 %). This finding is in line with literature data on alkaline paper, where such a trend was ascribed to water saturation of paper at high humidity content of the atmosphere.

The rate constants measured in the present work fit fairly well a recently modelled dose-response function, which quantitatively describes the degradation rate constants as a function of environmental factors and pH of the paper.

Therefore, it can be concluded that the recycled and non-recycled paper considered in the present study degrade with similar rates. The length and type of the fibre, the processes in papermaking and overall quality of the resulting paper, which can make these two kinds of paper very different from various points of view, do not seem to influence their degradation kinetics. In addition, it is interesting that the equation originally modelled for historical paper, and thus specifically devoted to the preventive conservation of historical collections, seems to give reliable predictions (within about the same extent of uncertainty as historical paper) also for both kinds of contemporary paper considered here. However, further results on a larger variety of recycled and non-recycled papers would be useful to corroborate the present findings.

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CHAPTER 3

NON-DESTRUCTIVE COLLECTION SURVEY AT THE CLASSENSE LIBRARY (RAVENNA, ITALY)

Abstract

This Chapter reports an innovative library survey conducted in September 2017 at the Classense Library. The broad context in which this survey is set, i.e., preventive conservation, and the differences between this survey and the collection surveys performed so far are discussed in the Introduction of this Chapter, where the major aspects of novelty are highlighted. The present survey combines recent findings of studies on paper degradation and characterisation reported in the literature, using for the first time damage functions in conjunction with modelled NIR data to inform future preservation policies.

The Classense Library is located in the urban area of Ravenna (Northern Italy) in a 16th-century building that currently houses a valuable and composite library collection, composed of incunabula, manuscripts and documents than have been collected over the centuries. Because of the different historical and cultural values assigned to the books, and different storage environments (controlled and non-controlled), the paper book collection of the Classense Library was considered as two separate collections. Overall, about 300 European books, dated from the 14th to the 20th century, were analysed. Visual assessment and NIR spectroscopy, with the support of chemometrics, were performed in a totally non-destructive and non-invasive way to characterise the paper collections, evaluate the current conservation state and predict their useful lifetime in several environmental scenarios. Both collections were characterised in terms of important chemical and physical properties, i.e.,

paper types, pH, DP, tensile strengths, contents of lignin, protein, rosin, and fillers as well as the presence of optical brighteners.

The measured properties are generally consistent with the development and chronology of papermaking processes. pH, gelatine and tensile strength values lead to believe that the rag paper books housed in the controlled environment are in a better conservation state than those housed in the non-controlled environments, likely because the former books are made of a better quality paper. In addition to evaluating the current condition of the book collections housed in the two storage environments, elaboration of pH and DP values through known damage functions allowed to obtain isochrones and demography plots which describe how different environmental scenarios can influence the useful lifetime of the collections. In agreement with the literature, groundwood paper books represent the main concern among the books analysed in all scenarios, other concerns being related to manuscripts or books which include hand-written notes, even if stored in a controlled environment.

3.1 Introduction

Over the last decades there has been an increasing awareness of the importance of assessing the conservation state of book collections before managing their preservation in museums, archives and libraries. Any library, museum or archive is concerned about the preservation of their most valuable and/or fragile collections. As outlined in Chapter 1, degradation of paper-based materials is a function of numerous parameters which can be endogenous and exogenous [1]. These parameters may involve not only chemical and physical properties of the paper itself (e.g., pH, sizing), but also storage and use conditions (e.g., T, RH). Preservation surveys of book collections [2–7] represent extensive efforts and attempts that have been made to evaluate the nature and extent of degradation of paper-based materials, get an insight into the existence of preservation problems, know the percentage of the books affected by these problems and/or display the effects of environmental conditions. Indeed, the results generated from such a survey should inform conservation policy and strategy, starting with environmental conditions, in agreement with the recent standard BS 4971 [8]. As reported in the next sections, most of the published preservation surveys have been conducted at research and university libraries rather than at historical libraries. This gives an outstanding feature of novelty and interest to the present survey from both the preservation and research points of views as, nowadays, preventive conservation is an option preferred to basic paper conservation techniques.

In order to preserve a varied and challenging group of materials, a comprehensive knowledge of their composition and structural qualities is required [8]. Therefore, when approaching the analysis of a single book or a book collection spread in time, it is fundamental to consider the developments in the papermaking process whereby derives the huge variability of paper types produced over the centuries, as described in Chapter 1. In this regard, given that the books analysed in the present survey are made of European paper dated from the 14th to the 20th century, it can be useful to recall briefly the most important changes concerning the European papermaking in that period.

In medieval times, the paper consisted primarily of beaten, soaked and macerated linen, hemp and cotton rag fibres. In Europe, the pulping process was often performed using hard water, containing lime, which contributed to the alkalinity and permanence of the resulting paper [9]. Gelatine sizing was applied by dipping the paper in a solution of gelatine. However, since the invention of printing with movable type in the 15th century, the demand for paper extremely increased to print the so-called incunabula. Around 1650, the addition of alum to the sizing was introduced to counteract biodeterioration, but the alum usually contained some residual sulfuric acid, thus reducing the paper stability [9]. The initially slow pulping process and conversion of pulp to paper became much faster and productive with the invention of the Hollander beater in 1680, although its pulping action resulted in shorter fibres. Then, since Sheele's chlorine discovery, bleaching processes with chlorine soon followed. By the 19th century, due to a great increase of paper demand, other sources of cellulose fibres were being explored [9]. Especially with the introduction of the Fourdrinier machine for the continuous production of paper, the use of wood as a source of paper fibres was implemented as well as chemical processes based on soda, sulphite and sulphate. Moreover, in that period, rosin sizing was added to the pulp. Unfortunately, some of these changes such as the decrease of gelatine and calcium carbonates [10] and the use of alum-rosin [1,9], resulted in a pH drop of the paper. Overall, the changes of fibre resources from cotton and linen rags to wood fibres, together with the papermaking processes, had significant adverse effects on the permanence and durability of paper materials, so that the paper produced between 1850-1950 is generally of very poor quality. It has been reported that in a typical Western repository, 70-80% of these documents are likely to be acidic and therefore prone to rapid deterioration, their useful lifetime being about a century, a couple at best. This is in stark contrast to paper produced before ca. 1850, the lifetime of which may be longer at least by a factor 10 [1,11,12]. Also for this reason, nowadays, there is mounting concern about the deterioration of book collections, for which preventive conservation is increasingly gaining importance. Before going into the details of the present survey and the description of surveys previously performed, it is worth focussing attention on what conservation and its preventive form mean.

The authoritative International Council of Museums (ICOM) defines the conservation as «all measures and actions aimed at safeguarding tangible cultural heritage while ensuring its accessibility to present and future generations» and identifies three kinds of conservation: preventive conservation, remedial conservation and restoration [13], each of these being targeted to future, current and past deterioration, respectively. Preventive conservation, in fact, is defined as «all measures and actions aimed at avoiding and minimizing future deterioration or loss. They are carried out within the context or on the surroundings of an item, but more often a group of items, whatever their age and condition. These measures and actions are indirect – they do not interfere with the materials and structures of the items. They do not modify their appearance» [13]. In other words, preventive conservation is intended to avoid and minimise future losses, improve cultural features and economic values of the heritage, including strategies, actions and judgments to balance heritage protection and public access [14]. As underlined in a recent review [14], the challenge of preventive conservation seems to be the achievement of an equilibrium among a number of aspects such as damage minimisation, users' comfort, free access and safety precaution, not to mention other activities (e.g., restoration, didactics, selling) increasingly proposed especially in museums. These aspects would require environmental parameters different from each other, and sometimes even contradictory. In addition, collection care needs a strict environmental control in terms of light, air temperature, relative humidity and pollutants, which often imply the use of air-conditioning or lighting systems with consequently high-energy consumption [15], in contrast with the recommendation of energy efficiency suggested by the British standard BPAS 198 [16]. It has been pointed out [17] that the reduction of energy costs and museum's carbon footprint are to be encouraged, and a larger tolerance of the thermo-hygrometric values may improve the environmental sustainability, when it can be done without damage to the collection.

Science and conservation activities have gone hand in hand since the diffusion of preventive conservation practices in museums. Actually, the so-called practice of "housekeeping", which consists in the maintenance and staff management to control indoor climate in residential homes, was already known in the 16th century. Since then the ideas and best practices of restoration and conservation were debated internationally, as proved by the publication of Athens and Venice Charters. In the early 1970's, a new field in the conservation discipline, that is, preventive conservation, emerged. De Guichen divided the development of preventive conservation into three phases, one for each decade from 1965 to 1995. In the first one (1965-1975) the awareness on the question arose, in the second one (1975-1985) the term was properly introduced into the debate, and in the last one (1985-1995) a strategy was designed [18]. In the past, the loss of cultural heritage was mainly associated with events such as fires, earthquakes, floods, but since the last 40 years environmental storage conditions have been considered equally crucial. The book entitled *The Museum Environment,* edited by Garry Thomson, first published in 1978 [19], is still recommended as a reference book for preventive conservation. In his book, specific environmental parameters are suggested for the collections of paintings housed in London's museums and for interpreting and selecting values for other climates and buildings. Although these recommendations were a point of reference for many museums and international standardisation committees, some doubts arose on the values suggested as optimal [14]. However, after the work of scientists such as Thomson [19], Cassar [20] and

Camuffo [21], the publication of a series of guidelines and numerous standards [16,22–26], constantly evolving, demonstrates that the environmental and risk management is assuming an increasingly important role in cultural heritage conservation. Furthermore, in a museum or library various kinds of artefacts, made of different materials, are often stored. For instance, museum collections can be made of metal, textile, wood, and other materials. Similarly, library collections also are composite: a volume is made of paper or parchment, but its cover could be made of leather or wood. The huge variety of materials is an issue which inevitably complicates the actions to be implemented for collection preservation. In line with the focus of the present survey and the overall thesis work, a brief outline of the standards adopted in Italy, along with the most recent and international standards, is reported below with particular attention to the conservation of paper-based materials and the recommended values of T and RH.

In Italy, in 1997 the standard UNI 10586 came into force, providing microclimatic[17] parameters (units and limits) for a correct conservation of graphic documents, defined as «information recorded on materials made essentially of paper or parchment»[18] [22]. Several environments of conservation are identified as, for instance, areas dedicated to storage and consultation, and those to reading and exhibition. In addition, the standard also suggests the thermo-hygrometric, lighting and indoor air quality values for graphic documents. In particular, in a storage environment T should be within 14 and 20 °C, with a maximum gradient between different positions or times (daily or seasonally) of ±2 °C, while RH should be in the 50-60% range, with a ±5% of acceptable fluctuations in different positions and times.

In 1999, the standard UNI 10829 became active in Italy, indicating guidelines for the microclimate monitoring, and the correct parameters in terms of T, RH and their maximum fluctuations, illuminance, maximum ultraviolet radiation and maximum amount of illuminance for each typology of artwork [23]. Given the different sensitivity to T and RH of various materials, the standard suggests suitable parameters for different material categories (e.g., textile, herbaria, ceramics, stone). The suitable thermo-hygrometric conditions for paper-based materials range from 18 to 22 °C for T and from 40 to 55% for

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[17] Microclimate has been defined as «the synthesis of the ambient physical conditions (e.g., time and space distributions, fluctuating values and trends, average and extreme values, space gradients and frequency of oscillations) due to either atmospheric variables (e.g., temperature, humidity, sunshine, airspeed) or exchanges with other bodies (e.g., infrared emission, heating, lighting, ventilating) over a period of time representative of all conditions determined by the natural and manmade forcing factor» [21].

[18] Translated from Italian into English by the author.

RH, maximum excursions of ± 1.5 °C and ± 6 % being suggested for T and RH, respectively. However, it is worth noting that another category, which includes archival documents of paper or parchment materials, manuscripts, printed books, and stamp collections, is mentioned. The objects belonging to this latter category should be stored at T between 13 and 18 °C within a 50-60% RH range with an acceptable humidity gradient of ±5%. Moreover, this standard specifies that the proposed values should be adopted if no other specific standard relevant to the topic is available. In this regard, in fact, this standard recommends that UNI 10586 [22] should be the relevant one for graphic documents on paper or parchment materials.

The Ministerial Decree dated 10th May 2001 developed by the Italian Ministry of Cultural Heritage and Activities [24] focuses on the importance of a correct management and conservation of the collection. Interestingly, the Ministerial Decree distinguishes the chemical and physical degradation from the biological one, values to prevent both of them being suggested. In addition to sensitivity classes for photostability, as far as biological attacks are concerned the decree identifies two different categories: paper, and manuscripts and books. As far as the chemical and physical degradation is concerned, the 19-24 °C range for T and the 50-60% range for RH are suggested for both categories. To prevent biological degradation of paper T should range from 18 to 22 °C and RH from 40 to 55%, with maximum excursions of 1.5 °C and 6%, respectively, whereas for manuscripts and books T should be less than 21 °C and RH within the 45-55% range, with maximum excursions of 3 °C and 5%, respectively. This decree also indicates that the curators of museums or libraries, after careful assessment of the conservation state of the collection, the geographical area where the museum or library is located, and the actual possibility of ensuring the constancy of the thermo-hygrometric values, should evaluate the most suitable conditions, which can be different from those reported.

A European Technical Committee for Standardisation (CEN/TC 346 - Conservation of Cultural Heritage) has been working since the early 2000s on the development of standards for museums, archives and historic building environments [27]. In this context, the European standard EN 15757 [25] deals with the suitable environmental conditions for hygroscopic materials such as paintings, books, textiles, and leather. Instead of considering strict ranges of RH, this standard focuses on the climate to which an object has been subjected for a significant period of time. The expression ‘historical climate’ defines the «climatic conditions in a microenvironment where a cultural heritage object has always been kept, or has been kept for a long period of time (at least one year) and to which it has been acclimatised» [25]. Although such an object has been stored for a significant period of time in a poor quality environment, it should be acclimatised to these conditions. In fact, rapid changes of the microclimatic parameters, even towards conditions generally considered suitable, may generate further damage. In light of this, curators should verify whether more damages may derive from keeping the object in its historical microclimate, or imposing new benchmark microclimate values [25].

The recent British standard BPAS 198 [16] takes both the correct conservation and efficient use of energy into consideration. After identification of the appropriate environmental conditions, the strategy which involves the maximum energy economy should be implemented, recalling also the necessity of specific requirements for the artwork category. As far as the latter point is concerned, three classes of artworks are identified in terms of their sensitivity to temperature, while the classes based on sensitivity to humidity are associated with two probable processes, i.e. hydrolysis and mould growth, which may occur at unsuitable humidity levels. Therefore, items are divided into three categories to identify their risk to undergo hydrolysis with certain humidity conditions, and other two categories of objects that may have mould risk [16].

The standard ISO 11799 [26], highlighting that no international standard specifically dealing with the storage of documents made of paper, papyrus or parchment existed, suggests that any archive or library should assess its holding to find out what may be the storage environment that covers their needs, outdoor environment being also accounted for in the overall assessment. To control RH and T usually energy driven machinery, such as heating, ventilating and air conditioning (HVAC) systems are used, but the standard proposes repositories as an alternative, whereby the building materials and structure may contribute to keep the climate at the desired level. Generally, it is suggested that humidity should be below the point for which microbiological activity occurs, that is above 60% of RH [26]. Low humidity levels may increase brittleness, the lowest acceptable humidity levels for long-term storage of archive and library materials being still under discussion [26]. However, in an appendix of this standard, a table reports that climatic room conditions have a fair suitability with a 16-23 °C T range and RH levels from 30 to 40% [26].

Finally, the recently revised standard BS 4971 [8], specifically devoted to the conservation of archive and library collections, indicates that the storage of mixed traditional collections, which may include T and RH sensitive materials (e.g., beeswax seals on parchment documents), should be designed to provide an environment that does not expose the materials to T above 23 °C (a cautionary maximum) and below 13 °C, with an annual average storage temperature lower than 18 °C. RH levels should be in the 35-60% range. This standards specifies that information about requirements for an appropriate building environment and monitoring control should be in accordance with the standard EN 16893 [28]. Interestingly, the standard also reports that, to ascertain the likely vulnerability of different materials, a survey of the collections should be undertaken and updated periodically. The results generated from such a survey should inform conservation policy and strategy, starting with environmental conditions [8].

As far as the gaseous pollutant concentrations are concerned, ozone (O_3), nitrogen oxides (NO_x) and sulphur oxides (SO_x) are cited as the most common contaminants from external sources, found in archival storage areas, in higher concentrations in urban areas [26]. However, only some of the standards mentioned above suggest threshold values of gaseous pollutant concentrations, most of them encouraging air ventilation and air exchange with appropriate air filtering systems. In this regard, to support the air quality monitoring in museums or libraries, the IMPACT model can be used [29]. This model estimates the building indoor/outdoor ratio of air pollutants concentrations, and hence the indoor concentration if the outdoor one is known. The level of contaminants that may have an internal source (such as acetic and formic acids) should be also evaluated. About NO_2, 10 $\mu g\ m^{-3}$ is indicated as threshold value in the standard UNI 10586 [22] although other values are reported in the Ministerial Decree [24]. In this regard, it is worth mentioning the approach proposed by Tétreault [30] for which different pollutant levels correspond to different preservation targets (e.g., 1, 10 or 100 years). The effects of pollutants on paper-based materials including NO_2 has been also reported by Menart and co-authors, as discussed below [31].

Finally, it is to be noted that all the above-mentioned standards suggest the implementation of what are considered the best environmental conditions to prevent artworks for further degradation, although they suggest somewhat different values. It is evident that the standards promote the assessment of suitability of storage environments considering thermo-hygrometric and air quality control. It is also pointed out that generally lowering T and/or RH will make the life of documents longer, high RH and T increasing deterioration processes as well as the risk for mould attack. However, there is still some debate about the optimal conditions. Besides, it can be more appropriate to keep the object in its historical climate rather than to force its adaptation to new conditions. Therefore, an accurate analysis of the state of the artwork, and of the suitability and regularity of the environmental conditions are two essential steps of a preventive conservation strategy, for which the cooperation of different professional figures is necessary. It is important to consider that although kinetic models suggest keeping T and RH as low as possible, it is necessary to account for other factors, such as the consultation of an object, or more generally its use, and possible damages deriving from water condensation. Therefore, a compromise between what is better for the object conservation and what is better for its use has to be reached. For instance, too low levels of T and RH would favour embrittlement of paper, thus determining conditions not suitable for use.

Efforts to slow degradation of paper-based cultural heritage to preserve its intellectual, historic, artistic, and economic worth have been made not only acting on the environment that surrounds the artworks, but also by means of practices such as deacidification. This word accounts for the treatment to which a paper-based material is subjected to neutralise its acidic content, with the aim of making the object useful life longer [32]. This procedure is also referred to as alkaline buffering, given that such a treatment may provide alkaline reserves, useful against possible future production of acids. Generally, mass deacidification programs, able to remove acidity from hundreds books at a time, were performed to reduce costs and efforts. Such treatments are presented in a review [32] as a promising strategy to slow the chemical mechanism of acid-catalysed hydrolysis, and thus slow the rate of paper degradation. In this case, the threat comes from the paper itself rather than the environment. In fact, as mentioned above, paper manufactured during about the second half of the 19th century to the second half of the 20th century is more acidic than that produced before, and thus more likely to need deacidification treatments. Weak bases, which include carbonates, bicarbonates, hydroxides, as well as amines, may be used for deacidification as indicated by the numerous patents listed by Cedzova and co-authors [33]. Immersion into solutions are the most frequently used aqueous conservation treatments, although for several types of documents (e.g., containing water-sensitive inks) non-aqueous deacidification procedures have been proposed. In general terms, a successful deacidification treatment should be able to neutralise paper acidity and provide alkaline reserve, without negative side effects, such as changing paper appearance or physical properties. In fact, it has been observed that some acid papers may be destabilized as a result of deacidification treatments [34]. Because of the sensitivity of library materials to water, and time and energy consuming drying processes, non-aqueous solvents are usually employed, in which for instance alkalis may be finely-powdered [35].

Furthermore, antioxidants and reducing agents, although their use can be closely linked to certain deacidification schemes, may be used with a different conservation function. These agents, in fact, act preventing further degradation induced by iron gall ink, that has been acknowledged as one of the major threats to the written cultural heritage. One of the most effective aqueous methods involves calcium phytate [36,37]. This method, developed by Neevel [38], consists in inhibiting oxidative decay with the complexing agent myo-inositol hexaphosphate (phytate), and subsequent deacidification using aqueous solutions of calcium bicarbonate. Alternatives have also been proposed as magnesium phytate [39]. Certain inks, especially iron gall inks, contain large amounts of iron and copper, leading to localised degradation which may reach such an extent that documents are no longer readable (see Figures 3.13 and 3.14). Actually, what is generally referred to as iron gall ink is characterised by a high chemical variability. Generally, this ink, often prepared by the writer himself, is a mixture of Fe(II) compounds, gallotannins, gum Arabic and water [40]. Such inks, although produced with many different recipes, represented the most common kind of ink in the West, being used from the early Middle Ages until the first half of the 20th century. Its instability, due to oxidation when exposing to air, which renders the ink insoluble, leads to decomposition (corrosion) of the cellulosic support [40]. Chemiluminescence analyses have shown that there could be possible formation and transfer of reactive oxygen species. Moreover, despite a less intensive emission of degradation products (i.e., volatile organic compounds), it has been proved that iron gall ink has a measurable negative effect on paper degrading in its vicinity [41]. pH and DP of areas with iron gall ink have been found to be lower than those of paper without ink application, supporting the corrosive effect of such inks [40]. Recently, it has been demonstrated that hydrolysis seems to be the dominant mechanism in ink induced degradation during natural ageing and, iron gall ink has been found to accelerate the rate constants of a factor equal to 1.59 [42]. In light of the latter findings, also the degrading effects of iron gall ink on paper are not negligible in the perspective of preventive conservation.

Finally, given that, as mentioned above, conservation means not only to preserve an object, but also to make it accessible and usable, it is worth mentioning that, according to a recent study [43], items are considered unfit when text is evidently missing. However, if the visitor/reader is prompted to think of a document in terms of its historic and cultural value, even large missing pieces do not make it unfit for some uses (e.g., documents intended to be displayed) [43].

3.1.1 Condition survey: literature review

Since the late 1970s, there has been an increasing attention to quantifying and understanding the preservation needs for academic libraries, museums and archives [44]. A collection condition survey has been defined as a logical and relevant starting point for preservation planning in any library [45] providing the most significant information relative to the development of a preservation program [46]. A study conducted in 1974, under the supervision of William Barrow, on almost 1500 paper books dated between 1507 and 1949 revealed new information about paper permanence and durability [47]. In the late 1970s and early 1980s, several libraries with pioneering preservation programs conducted surveys of their collections in an attempt to determine their overall condition and prioritise preservation actions. In 1979, the Stanford University conducted a survey at the Green Library [3] determining the percentages of its collection that were in good (32.8%), moderate (40.8%) and poor (26.5%) condition. The methodology developed by the Stanford survey represented a landmark that has proven useful for other libraries. A study carried out at the Yale University Library [2], one of the first large-scale surveys of the physical and chemical conditions of books, was aimed at determining the extent and nature of book deterioration. It was found that about 37% of book samples had brittle paper and about 83% had acidic paper. A few years later, a similar percentage of acidic volumes was found at the Syracuse University Library [4]. In 1988 a Swedish study [48], one of the earliest European condition surveys, estimated that the proportion (20%) of books with paper in the worst state was approximately the same in the National Archives of Sweden, Royal Library and Uppsala University Library. These books were mainly printed from 1860 to 1890, i.e., just after the diffusion in Europe of mechanised rosin sizing. Similar studies estimated that about 30% and 40% of the collections at the Library of Congress (Washington, DC) and Harvard University Library, respectively, are in such a state that they can no longer be used by the public [48]. Although several methodological aspects of such condition surveys can differ considerably (e.g., sampling strategy, analysed collections, performed tests), most of these provided alarming results about the condition of the collections.

The above mentioned surveys were mainly concerned with identification of the following features: amount and type of physical damages, percentage of books with acidic paper, and with embrittled paper. The importance of the last two features stems from the established correlation between acidity and longevity, and the limited accessibility of brittle items. However, as reported by Brown [49], the main and more general interests of such surveys were to prepare preservation plans, and improve storage practices and environments. In this regard, among those institutions interested in improving the storage environment as a goal of the assessment, more than 52.4% succeeded in improving or installing environmental controls, and about a half improved or installed environmental monitors [49]. Therefore, especially over the last decades, such condition surveys have represented a very useful tool for preventive conservation, minimizing future deterioration or loss, without interfering with the materials and structures of the items. This kind of surveys is important for libraries involved in long-term preservation policies to design preservation programs, suitable to address current and future needs of their collections [50].

Depending on the type of collections and the needs of libraries, surveys may be item-level, best to establish treatment priorities, or based on a random sample, best to develop preservation programs [51]. Compared to the latter category, item-level surveys are much more time-intensive. Although both kinds of survey have been reported in the literature, far more sample surveys have been documented. Identifying the sample of books within a library collection can occur in many different ways, and it seems that each survey created its own unique process, as long as it is random and representative of the population [50]. Green [52] listed several sampling methods used in such surveys: 400 samples over the whole collection regardless of the population size; 1% of the stock, not selected randomly but only damaged items; every 10th item on each shelf; 1000 items for each category of material. The stratification strategies as part of the sampling method may also be different. For instance, Walker and co-authors [2] stratified their sample by library units, while Bond and co-authors [4] sampled a proportionate number of books from each sub-collection using random numbers to identify items on the shelves, and again Barrett and co-authors [10] distributed the sample by country and date of publication.

Much of the literature addresses surveys carried out on university and academic collections [2,4–6,45,50,53–58], while only a few surveys were performed at national or public libraries [7,48,56].

Additionally, most of the condition surveys that have been performed so far involved destructive and/or invasive tests on books: pH was often measured by means of pH-indicator pens (e.g., Abbey pen), while the brittleness of paper was evaluated through fold tests, where a corner of a text block page was folded back and forth (once, twice, or more) with possible consequent breaks [2,4–6,45,50,53–57]. The analytical methods which do not use chemicals or solvents are becoming rightfully preferred for the analysis of historical artworks. The use of destructive and/or invasive methods constitute a severe limit to their application to historical materials. Indeed, much of the literature in this field reports surveys of paper materials (e.g., monographs, periodicals) from 1800 until present, while only a few condition surveys of paper material dated before 1850 have been published. Teper and Erekson [51] surveyed the physical condition of a specific uncatalogued backlog of 16th- and 17th-century books with a visual assessment of binding, cover materials, board, spine, cover and text block conditions and embrittlement, without measuring paper acidity. Interestingly, a recent research conducted at the University of Alaska Fairbanks [58] reported that a double fold test was initially considered to examine paper brittleness, but the curator ultimately decided against it because the test would cause damages to the books, so that no strength tests were performed. However, in this regard, it is worth mentioning a research that has been conducted non-destructively on more than 1500 paper books, dated between the 14th and 19th centuries, at the Newberry Library and University of Iowa Libraries [10]. This analysis was undertaken to understand changes in paper composition over time and how these variations might affect paper stability. Spectroscopic techniques were involved such as X-ray fluorescence (XRF) to measure Ca, K, S and Fe, and ultraviolet/visible/near-infrared (UV/Vis/NIR) spectroscopy to evaluate colour and gelatine concentration. In particular, the latter was estimated through the development of a chemometric model using NIR, calibrated with gas chromatography/mass spectrometry. In Barrett and co-authors' research [10], European papers were predominantly analysed. Actually, several aspects, such as the implementation of non-destructive techniques (especially NIR spectroscopy), the analysis of historical and modern books, and the European origin of these books made the study of Barret and co-authors similar to the present study. However, as outlined in the next sections, in addition to the characterisation of paper through a variety of chemical and physical properties supplied by the SurveNIR, one of the aims of the present survey consists in modelling possible future scenarios of book conditions in relation to different environments (controlled and non-controlled) in the perspective of preventive conservation.

3.2 Aim of the study

The present survey, developed as a joint collaboration with the Institute for Sustainable Heritage of the University College of London[19], was carried out to evaluate the conditions of the collections housed in the Classense Library in terms of the main chemical and physical properties, such as pH, DP, tensile strengths, contents of lignin, rosin and protein. The state and nature of the deterioration of two book collections stored in two different environments (and with different historical and cultural values) were compared. Isochrones and demography plots, obtained with the pH and DP values supplied by the SurveNIR, allowed to evaluate how the current storage scenario and possible modified scenarios may influence the useful lifetime of the collections, thus providing information necessary for evaluating possible preservation actions.

3.3 Materials and Methods

3.3.1 Classense Library and its collections

The Classense Library (Biblioteca Classense, in Italian) is located in the urban area of Ravenna (Northern Italy) in a 16th-century building, the Camaldolese abbey, originally designed as a monastery, and then officially converted into a library in the 18th century. Over the centuries, the building has undergone several changes of use and enlargement works, up to the current extension of 28.000 m^2. Its origins as a library and the first enlargement works are dated back to the end of the 16th century, when the Library collection counted about 60 documents and new spaces were designed by the architect Giulio Morelli

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[19] The Classense project was elaborated by Floriana Coppola with the supervision of Prof. Alberto Modelli and Prof. Matija Strlič during her visiting period at UCL (Feb-Aug 2017). Data collection was carried out by Floriana Coppola and Natalie Brown. For the purposes of our theses and publications data ownership and research outputs of the collaboration have been summarised:

- The following data are jointly owned by Floriana Coppola and Natalie Brown. Each student is able to use these results within their PhD thesis independently with reference to the role of the other student.
    - NIR data collected during Sept 2017 Classense survey (NB collected)
    - Visual assessment data collected during Sept 2017 Classense survey (FC collected)
    - Metadata (i.e., year of publication) of the surveyed books collected during Sept 2017 Classense survey and through library's digital and paper catalogues (FC collected)
- Two publications will be generated from the surveyed data, to be written collaboratively after the submission of our theses in Oct 2018:
    - Part 1 will concentrate on the collection survey in its present condition. A first draft has been written by Floriana, Natalie will continue working on this draft and will be the first author of this publication.
    - Part 2 will concentrate on the future condition of the collection through modelling. Floriana will be the first author for this publication.

[59]. Since then numerous books were collected thanks to the acquisitions obtained by the abbot Pietro Canneti and father Mariangelo Fiacchi, such as the incunabulum *Biblia latina* printed on parchment by Nicolas Jenson in Venezia in 1476 (BCRa[20], Inc. 31), and the parchment manuscript *Libro d'ore*, dated at the end of the 15th century (BCRa, Ms. 4) [60]. The spaces were soon not enough to allocate the numerous volumes, so that upon request of Pietro Canneti, the architect Giuseppe Antonio Soratini started building the so-called Aula Magna in 1707 [59]. In 1798 a Napoleonic decree suppressed the libraries managed by religious orders. Then several administrations succeeded, until in 1803 the judicial system elected the Library as Public Library of Ravenna, in which also numerous books and entire collections from religious and private libraries had to be housed. It has been reported that in 1851 the Library housed 50.000 documents [59]. The need of larger areas led to new enlargement works, that went on until few years ago. The Library still provides evidence for the different architecture styles: going from the 16th-century Refettorio, at the ground floor (refectory of the original abbey) where it is possible to admire the fresco *Le nozze di Cana* of Luca Longhi (1507-1580), recently restored, trough the 17th-century Corridoio Grande (a corridor), at the first floor, where paintings of Giovanni Battista Barbiani represent Saints of the Camaldolese order, to the impressive 18th-century Aula Magna, finely decorated with frescos, oil paints, marble statues and carved wood shelves [60]. Currently, the building includes three levels and numerous rooms where items are stored, some of them freely open to people and others accessible in a dedicated room upon request. In addition to the outstanding paintings and artworks that still decorate the library rooms and corridors, the Library preserves one of the most valuable Italian collections. The wide collection of items made of different materials includes ancient and modern printed works, paper and parchment manuscripts, incunabula, etching, maps, photographs, archive documents and multimedia materials, acquired over centuries from several religious orders, private collections, donations and acquisitions [61]. However, in order to evaluate the current conservation state of paper-based collections using the SurveNIR system, the present survey focuses only on catalogued paper materials, namely manuscripts, incunabula and modern printed books, other kinds of items (e.g., letters, parchment manuscripts, geographic maps) being not considered regardless of their remarkable value. Numerous paper items have been classified by the curators of the Library as high value objects because of their rarity. These items have been stored since 2012 in a dedicated room (hereinafter

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[20] BCRa is an acronym which stands for Biblioteca Classense Ravenna.

named Caveau), accessible only to the library staff, where T and RH are mechanically controlled. The remaining paper items considered in this survey are stored in several rooms on different floors (e.g., Aula Magna, Sala delle Scienze, Sala Santi Padri, Sala Dantesca) where the thermo-hygrometric conditions are not controlled, being thus characterised by notable seasonal fluctuations. Figure 3.1 shows the current layout of the Classense Library, where some rooms of interest are marked with letters.

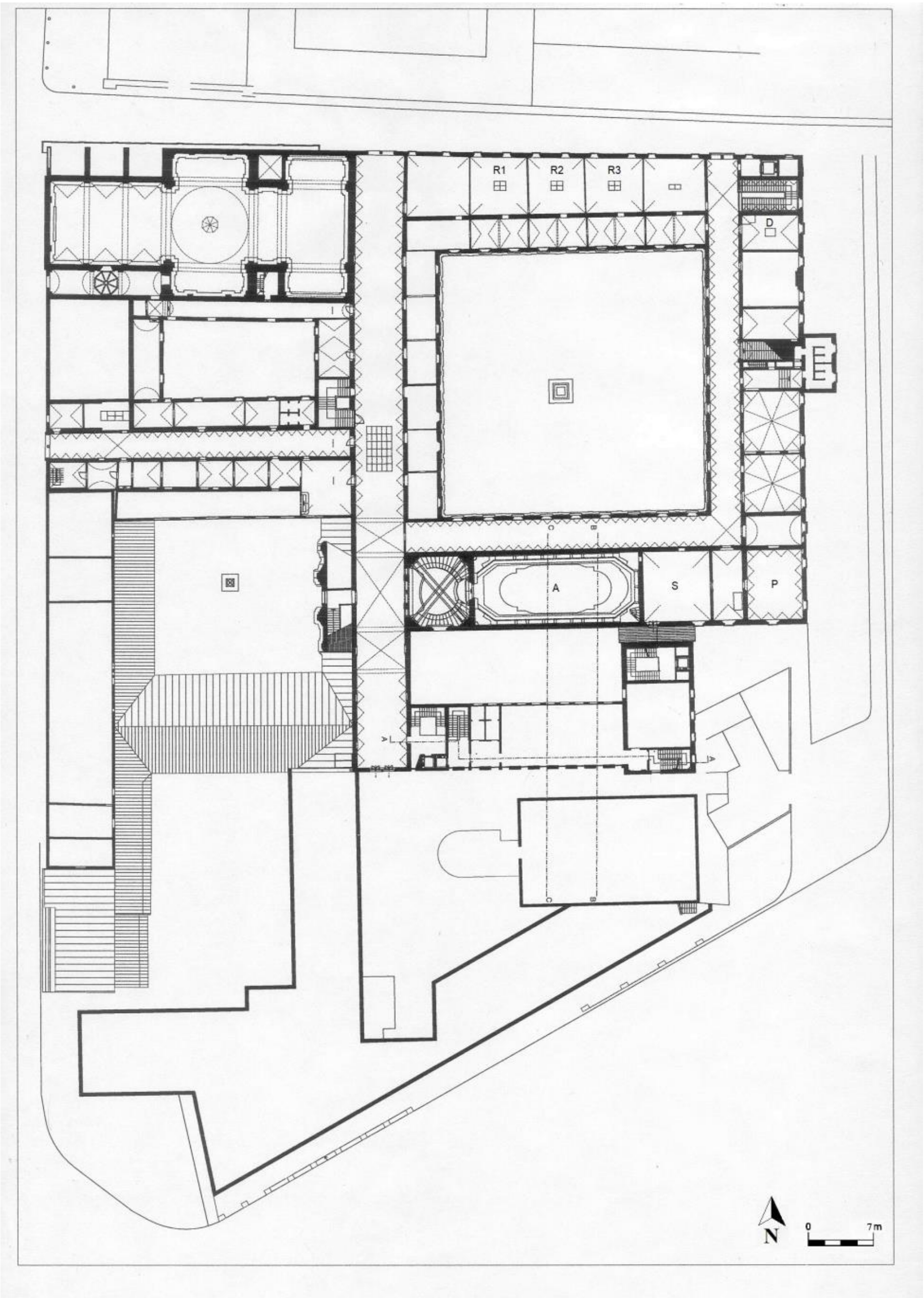

Figure 3.1. Classense Library layout. The letters indicate the rooms at different floors where the books of interest are located: A (Aula Magna – second floor), S (Sala delle Scienze – third floor), P (Sala dei Santi Padri – third floor), D (Sala Dantesca – third floor), R1, R2 and R3 (storage rooms – first floor).

Similar condition surveys had never been performed at the Classense Library, so far. Because of the different cultural and historical value assigned to the books and their environmental storage conditions, this survey considered two separate collections:

- C collection, including books of remarkable worth stored in the controlled environment (Caveau);
- NC collection, including books less precious (although some of them are dated back to the 16th century) stored in the non-controlled halls of the Library.

Figures 3.2-3.4 show photographs, taken during a preliminary inspection at the Library, of the rooms and shelves where the analysed books are stored.

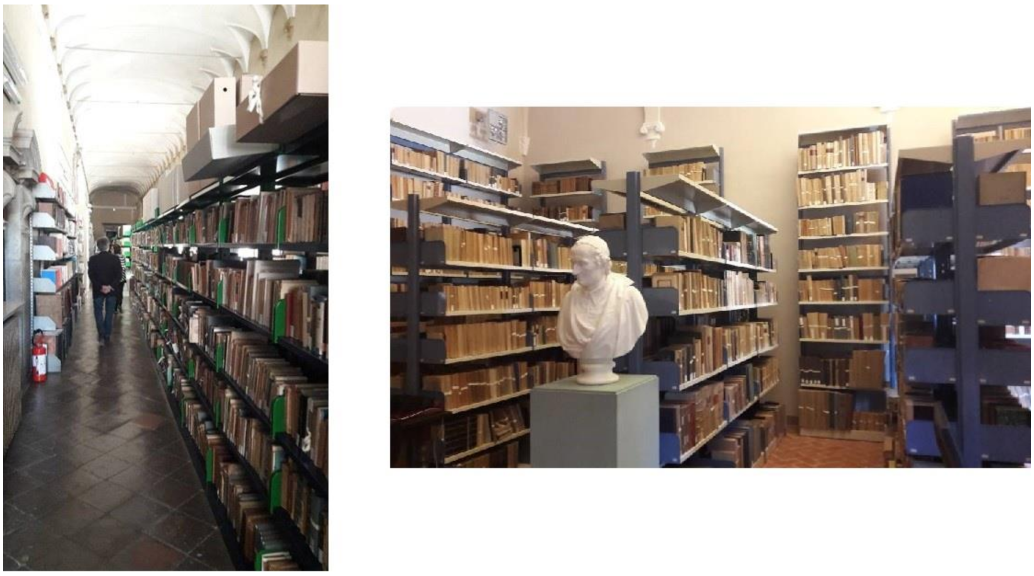

Figure 3.2. Storage environments on the first floor. Left: corridor. Right: storage room.

Figure 3.3. Storage environments on the third floor. Left: Sala dei Santi Padri. Right: particular of wood shelves protected by metallic nets in the anteroom of Sala dei Santi Padri.

Figure 3.4. Aula Magna with open shelves on the second floor.

Both in the controlled and non-controlled environments, most of the items are stored on open shelves, a few shelves being covered with glasses or metallic nets. The available paper and digital catalogues of the Classense Library allowed to evaluate the number of items of interest for this survey.

The C collection is characterised, as mentioned above, by items of remarkable cultural and historical value. In particular, the overall C collection groups about 1200 items, including about 400 manuscripts from the 14th to 20th century, and about 800 incunabula from 1465 to 1500 [62–65]. It consists in a composite collection made of paper and parchment books, miscellanea, with leather, wood, or parchment covers. As far as the parchment materials are concerned, in addition to *Biblia latina* (BCRa, Inc. 31) and *Libro d'ore* (BCRa, Ms. 4), other objects are worth to be mentioned: the famous manuscript of *Commedie* by Aristophanes, written in the mid-10th century (BCRa, Ms. 429); the incunabulum *Naturalis Historia* by Pliny the Elder, printed in Venice by Johannes de Spira in 1469 (BCRa, Inc. 670); the manuscript *Canzoniere e Trionfi* by Francesco Petrarca, dated at the end of the 15th century, which includes an outstanding illustration of *Trionfo d'Amore* attributed to Sandro Botticelli (BCRa, Ms. 143). Some examples of precious books analysed in the present survey among the C collection are: *De oratore*, printed in Subiaco by Conrad Sweynheym and Arnold Pannartz, dated 1465, the first Italian incunabulum (BCRa, Inc. 213); one of the first illustrated versions with xylographies of the *Commedia* by Dante Alighieri, dated 1487, printed in Brescia by Bonino Bonini (BCRa, Inc. 769); four volumes of the miscellanea *Consiglia et allegationes variorum iurisconsultorum*, dated between the 14th and 15th century (BCRa, Ms. 485); and the manuscript *Astronomica*, dated 1483, by Basinio da Parma (BCRa, Ms. 120).

The overall NC collection includes about 54000 items of interest for this survey, about half of which are books printed from the 16th to the 19th century, the other half being dated between 1901 and 1950 [66].

3.3.2 Sample size and sampling strategy

M. Carl Drott in his pioneer article [67] for understanding methods of random sampling of library materials stated that sampling is a compromise measure, but it is also an important management tool if one is faced with both need for information and limited time and money resources. The sampling strategy followed in this survey considered the C and NC collections as two separate populations.

The sample size for the NC collection, which counts about 54000 items, was calculated according to the following formula [68]:

$$\mathrm{n_0} = \frac{\mathrm{Z^2 * p * (1-p)}}{\mathrm{d^2}} \qquad \text{(Eq.3.1)}$$

where:

$\mathrm{n_0}$ is the sample size;

Z, or Z-score, corresponds to the chosen confidence level;

p is the proportion in the population possessing the characteristic of interest, expressed in decimal form[21];

d is the tolerance, expressed in decimal form.

For the C collection, given that the population N_p, which counts about 1200 items, is not large enough with respect to the sample size $\mathrm{n_0}$ (that is, $\mathrm{n_0}/\mathrm{N}_p \geq 0.05$), the finite population correction was considered [68]. Therefore, the sample size was recalculated according to the following equation:

$$\mathrm{n} = \frac{\mathrm{n_0}}{1+\frac{\mathrm{n_0}-1}{\mathrm{N}_p}} \qquad \text{(Eq. 3.2)}$$

where:

n is the sample size with the finite population correction;

$\mathrm{n_0}$ is the sample size calculated using Eq.3.1;

N_p is the population size.

---

[21] When a better evaluation is not possible, p may be set equal to 0.5, since in the formula it yields the maximum value of n. This procedure will give a sample large enough for the desired reliability and interval width [68].

Due to time and resources availability, the interval of confidence and the tolerance chosen were 95±10%, so that the sample sizes resulted to be 96 items for the NC collection and 89 items for the C collection, using Eq. 3.1 and Eq. 3.2, respectively.

As mentioned above, the common sampling technique called stratification occurs in different variations (e.g., collections, buildings) in most studies and throughout the condition survey literature. Stratification allows more accurate samples to be selected by creating sub-groups (strata) that are more homogenous than the entire population [50]. In this survey, given that both collections spread in terms of time, strata of items grouped by publication date were elaborated. As far as the strata sample sizes are concerned, different methods can be followed [50]. As an example, one method consists in treating each stratum as an entire population; another one, the so-called proportional strategy, divides the overall population sample proportionally to the number of items of each stratum; according to another one, the so-called uniform strategy, the sample size is divided by the number of the strata. The latter two methods evidently lead to much smaller sample sizes than the first one.

In the present survey, information on the total number of books and publication dates for both collections is partly missing. The data available on the Classense catalogues were used to evaluate the sample size for the entire collection (population) and for each stratum. According to the proportional allocation strategy, a few items (i.e., one or two) would have been surveyed in the most ancient strata, while with a uniform allocation (that is, the same number of sample books for each stratum, regardless of its size) these ancient strata would be more represented. Therefore, with the aim of assessing also the least numerous strata, the sampling strategy implemented in this survey resulted from a comparison between the stratified uniform and proportional strategies: the number of books sampled in each stratum was the highest one between the two indicated by the proportional and uniform allocation procedures. The adoption of this mixed strategy allowed to analyse also the least numerous strata. Eventually, a total of 297 items were analysed: 145 items of the C collection and 152 of the NC collection. The rapidity of the SurveNIR measurements allowed to analyse more books than those indicated by our mixed sampling strategy. Tables 3.1 and 3.2 report the sample size of each stratum in the two collections using different sampling strategies, and the number of the items analysed.

Table 3.1. Sample size as the number of items of each stratum for the C collection using different sampling strategies, and the number of the items analysed.

Collection C				
Stratum	Proportional strategy	Uniform strategy	Mixed (see text) strategy	Analysed books
1351-1450	1	13	13	14
1401-1500	7	13	13	16
1451-1500 (Incunabula)	58	13	58	60
1501-1600	4	13	13	16
1601-1700	7	13	13	17
1701-1800	11	13	13	14
1801-1900	1	8	8	8
total	89	86	131	145

Table 3.2. Sample size as the number of items of each stratum for the NC collection using different sampling strategies, and the number of the items analysed.

Collection NC				
Stratum	Proportional strategy	Uniform strategy	Mixed (see text) strategy	Analysed books
1501-1550	2	11	11	12
1551-1600	5	11	11	12
1601-1650	2	11	11	12
1651-1700	2	11	11	12
1701-1750	5	11	11	12
1751-1800	7	11	11	12
1801-1850	7	11	11	12
1851-1900	17	11	17	18
1901-1950	49	11	49	50
total	96	99	143	152

It is to be noted that the stratum sizes in terms of years of the C and NC collection are different. Indeed, the strata were elaborated separately for each collection because of a different accuracy of the publication dates for the two analysed collections. In fact, according to the Library catalogues the uncertainty of the publication dates for the C collection (excluded the incunabula that can be dated with an accuracy of a year) is about a century, while all books of the NC collection can be dated with an accuracy of a year. Therefore, as reported in Tables 3.1 and 3.2, the C collection was subdivided into 6 strata each covering a 100-year period, plus 1 stratum of 50-year. It is worth noting that the latter stratum formed by incunabula was considered as a separate stratum since all other items in the C collection are manuscripts. The NC collection was divided in 9 50-year strata.

As the Library did not have an adequately comprehensive list of volumes from which randomly select books, the curator, Dr. Floriana Amicucci, the person most knowledgeable about the locations of the books of interest at the time of the survey, randomly selected volumes from the shelves at different floors and rooms.

3.3.3 Non-destructive and non-invasive analyses

As mentioned above, since the late 1970s some condition surveys were carried out on academic collections using a fairly straightforward, but destructive, manual fold test, where a page corner is folded as many times as it takes for it to break off when gently pulled. Moreover, pH-indicator pens were invasively employed to measure the acidity of the paper, producing permanent stains, coloured or not, on the pages.

In the analysis of cultural heritage materials, destructive or only invasive methods are becoming more and more limited, non-destructive approaches being strongly encouraged and commonly allowed. In this survey, due to the cultural value of the collections examined, the curators and conservators of the Classense Library explicitly imposed the condition that no destructive and/or invasive methods had to be used. Therefore, two kinds of analysis were performed on each item in a totally non-destructive and non-invasive way: visual assessment, and NIR measurements. These analyses were carried out in a dedicated room, under ambient conditions, where the books to be analysed were delivered by librarians.

3.3.3.1 Visual assessment

An appropriate Excel spreadsheet was prepared to gather and record information about different features of each book. Firstly, bibliographic information, including author, title, date of publication, shelf location and book number, was recorded. Then, a visual assessment was conducted to gather information about the structural conditions of the binding, cover and spine (e.g., board detached, sewing broken) and of the text block, including observations for mould, stains, inks, water damage, pests, missing pages or parts, tears, detached or adhered pages. The amount and position (e.g., corner, along the spine) of tears and missing parts were recorded, as well as if the missing parts contained text. This latter aspect was considered of interest for this survey, as missing pieces influence readers/visitors' subjective judgments of fitness-for-use to a greater extent than do discolouration and tears, which have little or no influence [43]. As far as ink is concerned, it was described in terms of type and transfer. The ink transfer through the page was evaluated assigning four levels: 1st level, no sign on the opposite side of the page; 2nd level, a fairly visible sign on the opposite side of the page; 3rd level, an evident sign with a possible hole on the opposite side of the page; 4th level, only the borders visible, with the rest of the paper corroded. Possible previous repairs, restoration interventions on the paper, cover or binding, and the use of envelope boxes were also recorded. In case of doubts about damages to be added in the visual assessment form, the assessors made the decision by consensus.

Additionally, several photographs of each item and its peculiarities were taken to check *a posteriori*, during the data processing phase, what had been written down in the visual assessment form. Figures 3.5-3.22 show some detected damages.

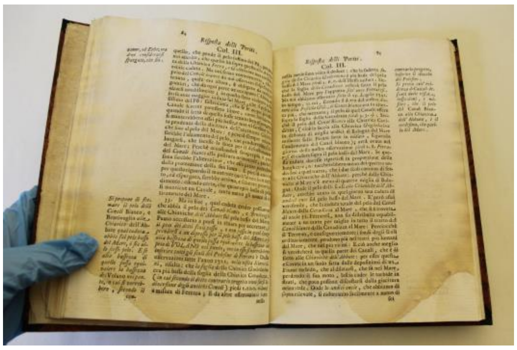

Figure 3.5. Picture of All'eminentissimo, e reverendissimo signore il signor cardinale Alesandro Albani prefetto della Sagra Congregazione dell'Acque (1742) with an extended water damage (BCRa, RAV. 078 004 K).

Figure 3.6. Picture of Aesopi Phrygis Fabellae Graece & Latine, cum alijs opusculis, quorum index proxima refertur pagella (1524) with an evident water damage (BCRa, CAM.A 006 002 T).

Figure 3.7. Picture of Consiglia et allegationes variorum iurisconsultorum (XIV-XV century) with purple stains related to mould (BCRa, Ms. 482, II).

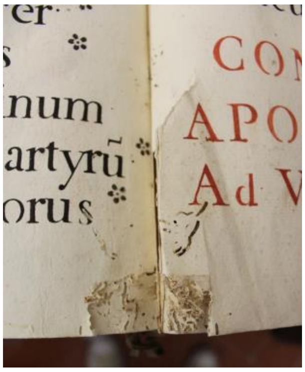

Figure 3.8. Picture of Hymnarium per annum ad usum S.Mariae Portuensis (1722) with evident signs of pest damage and a tear across the page (BCRa, Ms. 591).

Figure 3.9. Picture of All'eminentissimo, e reverendissimo signore il signor cardinale Alesandro Albani prefetto della Sagra Congregazione dell'Acque (1742) with an extended water damage and repair on the back of the title page (BCRa, RAV. 078 004 K).

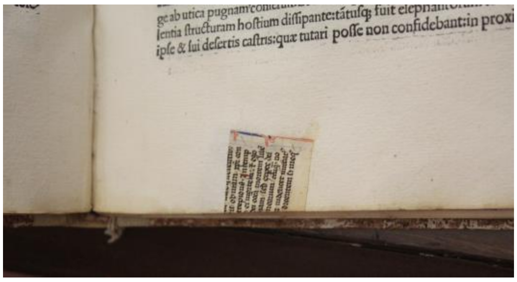

Figure 3.10. Picture of De primo bello Punico (1498) with a repair of the border page with a strip of paper with text (BCRa, Inc. 557).

Figure 3.11. Picture of Hymnarium per annum ad usum S.Mariae Portuensis (1722) with a tear across the inner part of the page (BCRa, Ms. 591).

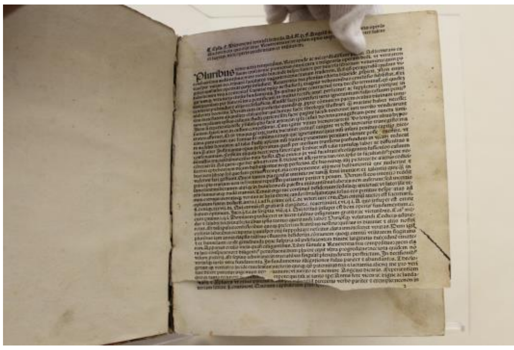

Figure 3.12. Picture of Summa angelica de casibus conscientiae (1489) with a missing piece including text (BCRa, Inc. 755).

Figure 3.13. Picture of Protrepticae orationes ad philosophiam (XVII century) with 4th level ink degradation (BCRa, Ms. 381).

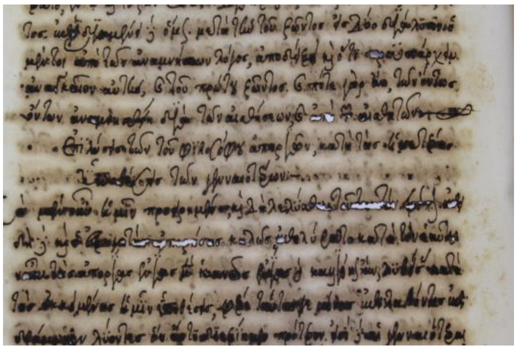

Figure 3.14. Picture of Delle leggi di Platone (XVII century) with 4th level ink degradation (BCRa, Ms. 380).

Figure 3.15. Picture of Opere di Giulio Perticari (1856) with the cover partially detached (BCRa, RAV. 003 003 060).

Figure 3.16. Picture of La guida dei seminaristi e dei giovani preti (1890) with a broken sewing (BCRa, MAZZ. F 0200 00985).

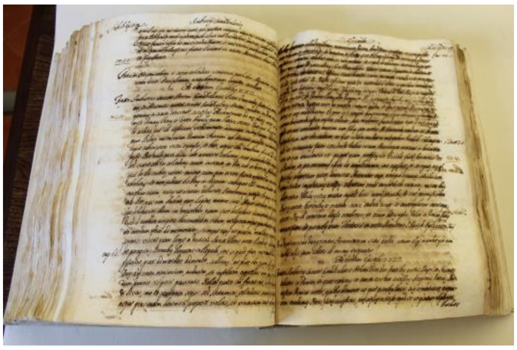

Figure 3.17. Picture of Epistolae Ambrosii camald. Gen. ex codice Bibliothecae Ambrosianae Mediolani procurante V. C. Iosepho Antonio Saxio (XVIII century) with 3rd level ink degradation (BCRa, Ms. 476, II).

Figure 3.18. Picture of Epistolae Ambrosii. camald Gen. ex codice Bibliothecae Ambrosianae Mediolani procurante V. C. Iosepho Antonio Saxio (XVIII century) with pages supported with Japanese tissues (BCRa, Ms. 476, II).

Figure 3.19. Picture of Hymnarium per annum ad usum S.Mariae Portuensis (1722) with pages adhered (BCRa, Ms. 591).

Figure 3.20. Picture of Principii di Diritto Costituzionale (1890) with border discoloration (BCRa, F. RAVA 23 01 26).

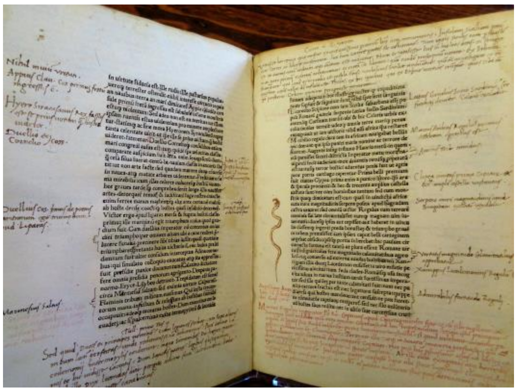

Figure 3.21. Picture of Epitomae rerum Romanarum (1475-1477) with different kinds and colours of ink (BCRa, Inc. 537).

Figure 3.22. Picture of De oratore (1465) printed in Subiaco by Conrad Sweynheym e Arnold Pannartz, first Italy's incunabulum, with the Library stamp and generic stains (BCRa, Inc. 213).

3.3.3.2 NIR Spectroscopy

In this survey, because of the mandatory use of non-destructive and non-invasive analytical techniques, infrared spectroscopy was identified as one of the most suitable techniques, mainly in conjunction with a recent important implementation of chemometrics. It is well known that infrared spectroscopy is of major importance in paper characterisation, covering different fields of application in paper analysis. IR spectroscopy allows to identify the origin of fibres and determine the chemical composition of additives used in papermaking [69–71]. In addition, many studies [72–78] have reported its important role in the study of paper deterioration processes. NIR combined with chemometrics has been used to study gelatine and other paper properties [10,79–81]. Indeed, NIR spectra exhibit low structural selectivity, in contrast to mid-IR and Raman techniques, and are characterised by overtones and combination vibrations, which mainly involve NH, CH and OH functional groups. However, as pointed out in the literature [10,79–81], in order to extract complex spectral information, instead of simple band assignment, a chemometric analysis of data is required. Models can be calibrated by comparing the whole or a part of the spectrum with chemical information obtained on the same set of samples, and then validated. For this purpose, partial least square (PLS) regression is often used to correlate spectral and chemical features [82–84]. In this survey, non-destructive NIR measurements were performed using the SurveNIR, a system based on chemometric models.

3.3.3.2.1 SurveNIR

The SurveNIR system (Lichtblau e.K, Dresden) consists essentially in a light reflection NIR-spectrometer and its dedicated user-friendly software, which allows extrapolation of data in formats editable with common software. This system has been proposed as an alternative to traditional destructive or invasive methods [85]. More than 1400 historical paper samples were destructively analysed in terms of fibre furnish, acidity, DP, tensile strength and tensile strength after folding, contents of lignin, gelatine and rosin, and other properties [85–87]. These reference data of all these paper samples were then correlated with NIR spectra to obtain chemometric models. Hence, this benchtop instrument enables to characterise the main chemical [79] and physical [80] properties of historical paper samples rapidly, non-destructively and non-invasively [85–87]. Figure 3.23 shows the SurveNIR tool.

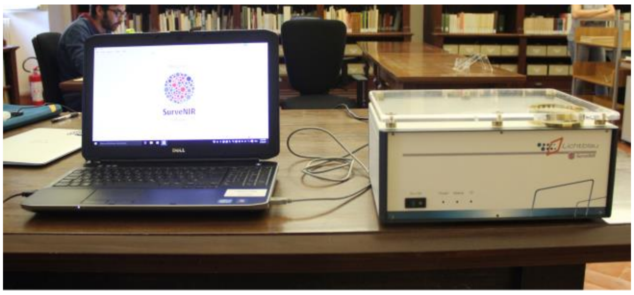

Figure 3.23. SurveNIR instrument with some accessories.

In the present survey, the reflectance spectra of all samples were collected in the interval of 1100-2200 nm with a 2 nm resolution. Eight measurements were taken on eight different pages of the books, along the borders, avoiding ink, stains and other possible evident source of errors. The spectra were automatically filtered and averaged by the SurveNIR software, and in case of ambiguous identifications 16 spectra were recorded. The measured variables were recorded in an editable format file (i.e., .csv), so that the data were processed with Microsoft Excel software. The chemical and physical properties of interest for this survey measured using the SurveNIR system were the following:

- Paper types: rag paper, bleached pulp paper (paper based on wood fibres but bleached with chemical processes, also known as ‘wood-free’), coated paper (from bleached pulp, ‘wood-free’) or groundwood paper (paper from mechanical wood cut, ’wood-containing’)
- Acidity (pH)
- Degree of polymerisation (DP)
- Tensile strength (TS) expressed in N

- Tensile strength after folding (TSF) expressed in N
- Lignin content expressed in mg/g
- Rosin content expressed in mg/g
- Protein content expressed in %
- Presence of optical brighteners
- Presence of Kaolin, Talcum and Gypsum

3.3.3.3 Time of the analyses

The survey planning started on March 2017 and went on with meetings and preliminary inspections of the Library. A proposal of the survey was discussed directly with the curator, Dr. Floriana Amicucci, and indirectly with the director, Dr. Maurizio Tarantino, in order to agree about three essential points: the number and kinds of items to be analysed, the duration of the analyses at the Library, the applicability of the results. In particular, the number of items and duration of the analyses had to be planned because the analyses on rare and historical items (i.e., all items of the C collection) were only possible when a librarian is present.

The analyses at the Classense Library started on September 4th and ended on September 26th. Visual assessment, photographs and NIR measurements were mainly carried out[22] by two PhD students (Natalie Brown and myself), sometimes with the supervision of Prof. Alberto Modelli. The presence of at least two people allowed to perform visual assessments and NIR measurements simultaneously, except for the analysis of some oversized books for which NIR measurements required both assessors. Thanks to a very useful preliminary work of pre-assembling the items to be analysed and the rapidity of NIR measurements, 297 items were analysed in about 49 hours, resulting in about 10 minutes per book. During the survey, the books analysed were handled with gloves. Figures 3.24-3.26 show the set-up employed for the NIR measurements.

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[22] See footnote 19 on page 101.

Figure 3.24. Preliminary discussions about the results of SurveNIR with the curator, Dr. Floriana Amicucci.

Figure 3.25. Handling an oversized book.

Figure 3.26. Experimental set-up for the analyses of books. Left: position for the visual assessment with the laptop for filling the form. Right: SurveNIR instrument with its dedicated laptop.

3.3.4 Statistical analysis

Different statistical methods were employed to characterise the surveyed collections. The matrix correlation and confidence intervals for the means of the available variables were calculated. Principal component analysis (PCA), probably the most popular multivariate statistical technique [88–90], was carried out using OriginPro 2017 (Origin Lab Corporation). The dataset was composed by all the variables measured in all the observations (i.e., the analysed books), except for the (non-measurable) DP values of groundwood paper. A multivariate analysis of variance (MANOVA), using the Wilks' lambda test [91], was performed with MATLAB R2016b (MathWorks) to verify if the differences between paper types and storage environments were statistically significant.

3.3.5 Environmental scenario modelling

Further elaborations of the data obtained from the SurveNIR tool provided very useful information to model and compare preservation plans achievable in various environmental scenarios. These elaborations were based on recent literature work [43,92–

94], especially the dose-response function modelled for historical European paper [94], and the results of a wear-out function [93]. Using these two functions, which describe paper degradation, isochrones and demography of the two collections analysed were elaborated.

3.3.5.1 Isochrones

Isochrone lines are the locus of points (each defined by a couple of T and RH values) for which the expected lifetime is equal. Isochrones are invaluable tools for analysing environmental conditions and their repercussions, so that they serve as a guide and provide a quick overview of the effects of RH and T on the stability of the collections. In addition, considering also the pH values, the results obtained with a deacidification intervention could be compared to those achieved with a continuous storage at cooler or more stable indoor conditions [94]. The isochrones were calculated grouping different kinds of paper as a function of their pH and DP values.

In order to evaluate the isochrones for each survival time (e.g., t = 50 years, 100 years), the corresponding rate constant was calculated using the well-known Ekenstam equation (see Eq. 1.14) [95], as follows:

$$\mathrm{k} = \left(\frac{1}{\mathrm{DP}} - \frac{1}{\mathrm{DP_0}}\right) \cdot \frac{1}{\mathrm{t}} \qquad \text{(Eq. 3.3)}$$

where k is the rate constant (year^{-1}); DP_0 and DP are the degrees of polymerisation measured and the threshold value for handling, respectively; t is the survival time (year).

In this survey, DP =300 was used as a threshold value of DP for the estimation of risk accumulation of missing pieces, reaching the end of fitness for use (i.e. reading/handling), as suggested by Strlič and co-authors [93]. Therefore, the rate constants calculated using Eq. 3.3 for each time (e.g., t = 50 years) was used to obtain the corresponding RH values, from T=5 °C to T=40 °C by 5 °C intervals, using the following dose-response equation [94]:

$$\ln(\mathrm{k}) = 36.981 + 36.72 \cdot \left(\frac{\ln(1-\mathrm{RH})}{1.67 \cdot \mathrm{T} - 285.655}\right)^{\frac{1}{2.491 - 0.012 \cdot \mathrm{T}}} + 0.244 \cdot \ln(10^{-\mathrm{pH}}) - \frac{14300}{(\mathrm{T}+273.15)} \qquad \text{(Eq. 3.4)}$$

where k is the rate constant (year^{-1}), RH the relative humidity expressed as a ratio, T the temperature (°C). Solving Eq. 3.4 for RH, it reads:

$$\mathrm{RH} = 1 - \mathrm{e}^{-\sqrt[\mathrm{i}]{\frac{\mathrm{x}}{\mathrm{y}} * \frac{1}{36.72}}} \qquad \text{(Eq. 3.5)}$$

where:

$$\mathrm{i} = \frac{1}{2.491 - 0.012 * \mathrm{T}}$$

$$x = \ln(k) - 36.981 - \ln(10^{-pH}) * 0.244 + \frac{14300}{T + 273.15}$$

$$y = -\left(\frac{1}{1.67 * T - 285.655}\right)^{i} = -\left(\frac{1}{1.67 * T - 285.655}\right)^{\frac{1}{2.491 - 0.012 * T}}$$

As an example, with pH=6.9, for t=50 year and k=$5.38 \cdot 10^{-5}$ year^{-1}, RH is estimated to be 99.4% at T=15 °C, and 82% at T=35 °C.

Potentially, isochrones could be developed for each book. However, in such a condition survey, it is useful to find values of pH and DP able to describe the whole collection or parts of it, when these parts differ considerably. For the following elaborations, pH was considered to be a key factor because of its well-known strong influence on paper degradation.

3.3.5.2 Demography of collection

Using the data measured with the SurveNIR system it was possible to forecast the effects of different environmental storage conditions on the time required for collections to become unfit for use (i.e., DP=300, when objects are no longer suitable for use). Looking at different environmental scenarios, it can be predicted how many objects of each collection will no longer be in a fit-for-use state in the long-term horizon of 500 years.

The above-mentioned wear-out function [93] allow to estimate the effects of frequency of access (i.e., use/handling). However, this function was modelled on documents with DP ranging from300 to 800, the rate of accumulation of wear and tears in documents with DP > 800 having a different dependence on handling. Given that, in this survey, only 4 books have DP < 800, as reported later, the effects of frequency of access (i.e., use, handling) were not taken into consideration.

To elaborate demography graphs for the two collections, first, the rate constant for each book was calculated using the dose-response equation Eq. 3.4 [94], accounting only for its pH value and environmental conditions (i.e., T and RH). Then, once the rate constant was known, the time to become unfit for use was estimated using Eq. 3.3 as follows:

$$t = \left(\frac{1}{DP} - \frac{1}{DP_0}\right) \cdot \frac{1}{k} \qquad \text{(Eq. 3.6)}$$

where again DP_0 and DP are the degree of polymerisation measured for each book and the threshold value (DP= 300) to become unfit, respectively. Therefore, demographic curves were elaborated only for the books for which DP was measurable, that is they were not elaborated for groundwood paper books.

3.3.5.3 Environmental monitoring campaigns

In the perspective of preventive conservation, environmental conditions surrounding works of art has become an essential information to well preserve an object from fast degradation processes. In the last three years, monitoring campaigns were carried out by means of thermo-hygrometric sensors and passive samplers, measuring T, RH and the concentrations of indoor nitrogen dioxide (NO_2) in order to describe the indoor microclimate of the storage environments of the Classense Library [96–99].

In summer [96,97] and winter [98], these measurements were carried out in halls where the environmental conditions are not mechanically controlled. The measured data showed a significant seasonal trend, especifically for the extreme values of T and RH, ranging from 7° to 28° C and from 51% to 71%, respectively. Indeed, the application of a relative risk assessment methodology (the so-called New rIsk assessment methodology for Cultural HEritage – NICHE) to the case-study of the Classense Library provided a medium risk for the values measured in summer [100].

As far as the controlled environment is concerned, a mechanical air conditioning system has been working since 2012 to keep constant T (20 °C) and RH (60%) values. It is worth noting that this room houses not only paper documents but also parchment materials of remarkable value, as mentioned above. Therefore, these thermo-hygrometric conditions have been considered to be the most suitable for storage of both paper and parchment materials. From the middle of January to the end of March 2017, the values of T and RH were measured in the Caveau, and resulted to have the desired values [99]. Table 3.3 reports the average thermo-hygrometric conditions and NO_2 concentrations measured in both environments.

Table 3.2. Averages of thermo-hygrometric conditions and NO_2 concentrations measured in summer and in winter in the halls without mechanical control system (NC environments) and in the Caveau (C environment), where the thermo-hygrometric conditions are mechanically controlled.

NC environments	**T (°C)**	**RH (%)**	**NO_2 (μg/m^3)**
Winter	13	65	5.2
Summer	27	56	8.5
C environment			
Caveau	20	60	5.0

3.4 Results and Discussion

3.4.1 Dates of publication

The dates of publication were gathered from the books themselves or, when not present, from the catalogues of the Library. As mentioned above, the accuracy of the date of publication is different between the two collections. The items of the NC collection were dated with the accuracy of one year, while among the C collection only the incunabula were dated with the same accuracy, most of others being classified as belonging to a given century. Figure 3.27 shows the sample distribution among the strata for both collections.

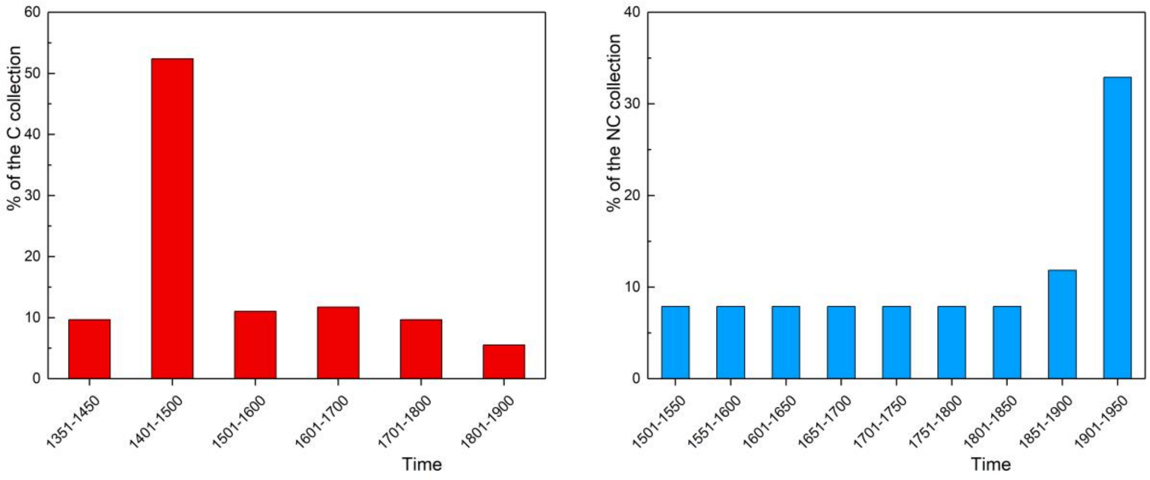

Figure 3.27. Distribution of the items analysed among the strata. Left: C collection. Right: NC collection.

The average and the median of the publication dates for the NC collection could be easily calculated, while for the C collection some assumptions were needed. In fact, for the books dated within a century the middle of that century was considered as the year of publication: for instance, the books of the stratum "1601-1700" were considered as dated 1650. Within the limits of this assumption, Table 3.4 reports the average and median ages estimated for the two collections.

Table 3.4. Average and median ages for the C and NC collections.

	Average age	**Median age**
C collection	1546	1494
NC collection	1784	1828

Information about the dates of publication, although the uncertainties for the C collection are large, is useful to comment and better interpret the results described in the following sections.

3.4.2 Visual assessment

Generally, damages to the structural conditions of the binding, cover and spine and to the text block can be mainly related to environmental damages (e.g., mould stains likely due to past/present unsuitable thermo-hygrometric conditions) and to handling/shelving damages (e.g., loose spine due to too tight shelving). Damages to books caused by environmental factors (e.g., water, mould, pests) indicate problems with physical housing, including building construction, environmental control, and housekeeping practices.

In the present study, the results indicated that damages were predominantly to the text block as opposed to cover, binding and spine parts, as shown in Figure 3.28.

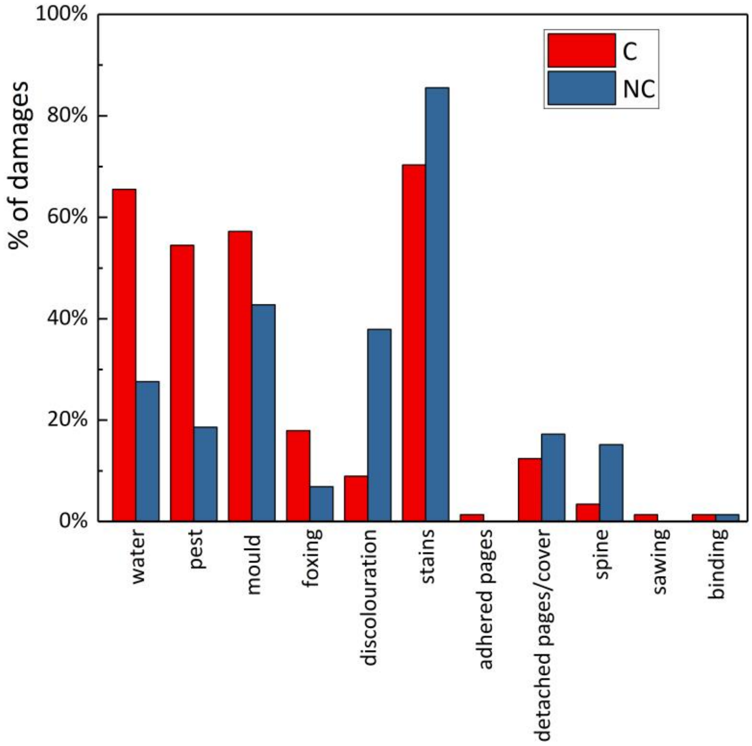

Figure 3.28. Distribution of damages detected during the visual assessment to the books of the C (red) and NC (blue) collections.

A high percentage of both collections showed evidence of staining, about 85% of the books of the NC collection being affected by stains. Moreover, it turned out that the most typical damages to the C collection, other than staining, are water (65%), mould (57%) and pests (54%), while other damages to the text block, such as foxing, discolouration and pages adhered to each other were noted less frequently. Structural damages to the cover, spine, sawing and binding were also detected, but at much lower rates, the most frequent of this kind of damages consisting in detached pages and cover (12% and 17% for the C and NC collections, respectively). However, these percentages should be interpret taking into account the number of books subject to previous repairs or restoration activities, reported below.

It is worth noting that the percentages of the books with the most recurrent environmental damages (i.e., water, pest, mould) are considerably higher in the C collection than in the NC collection. On the contrary, as far as the discolouration damage (evaluated from the borders darker than the centre of the page, see Figure 3.20) is concerned, this type of damage has more evidence in the NC collection than in the C collection. In agreement, the 19th- and 20th-century books of the NC collection contain wood-derived pulp (as reported below) which is well known to be more sensitive to yellowing.

The results of the visual assessment reveal also that the percentage of books with tears is higher in the C collection than in the NC collection. Figure 3.29 shows the percentages of books with no, few and frequent tears throughout the text.

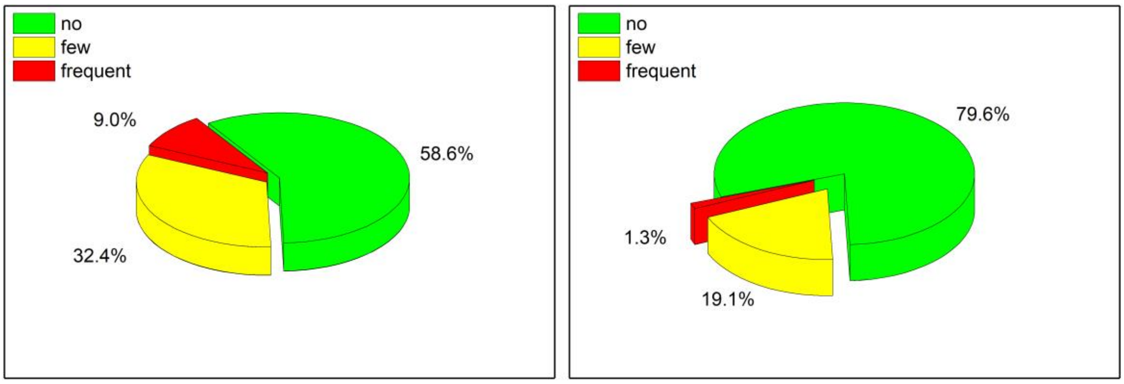

Figure 3.29. Percentages of books with tears. Left: C collection. Right: NC collection.

The relatively high incidence of tears in the C collection (about 41%) in the text block is comparable with that reported by Teper & Erekson [51] for 16th- and 17th- century books.

In the visual assessment form, the position of the tears was also recorded with the following options: edges, corners, centre of the page, along the spine, multiple tears. The latter label indicates books with tears localised in several parts. The identification of tears extending into the text (i.e., centre of the page) is significant because of a potential loss of information. Figure 3.30 shows the percentages of tear position for the C and NC collections.

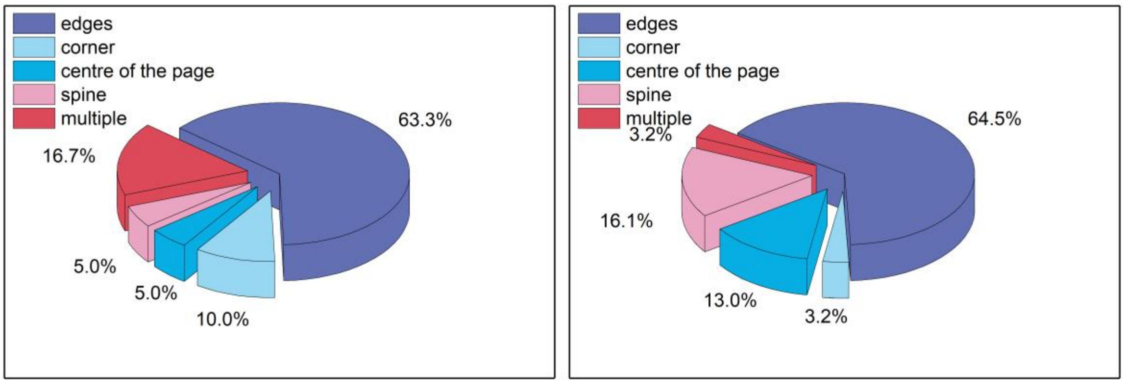

Figure 3.30. Distribution of the tears. Left: C collection. Right: NC collection.

It is worth noting that in both collections most of the tears are localised along the edges, only 5% (C collection) and 13% (NC collection) being extended to the text (i.e., centre of the page).

The identification of pages with missing pieces is a useful information as large missing pieces including text make a document unfit for use, unless the document has a strong historic value, in which case such deterioration is generally viewed with more tolerance [43]. Figure 3.31 displays the percentages of books with missing pieces, including or not some text.

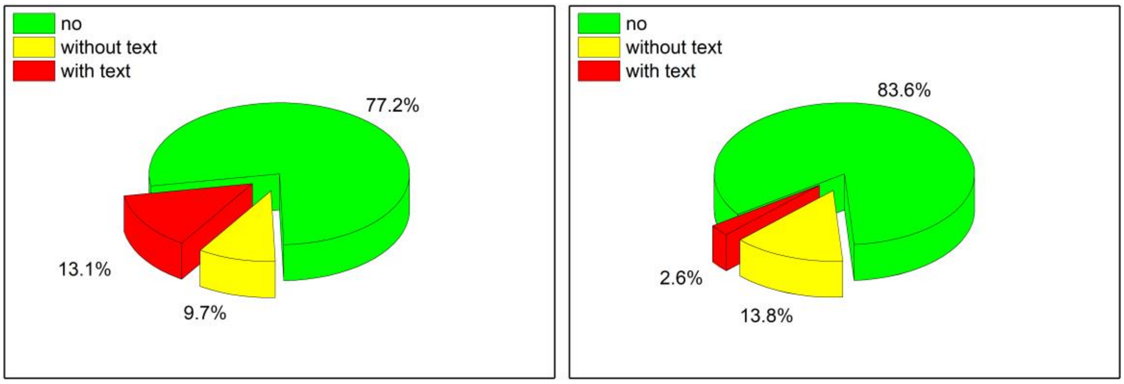

Figure 3.31. Percentages of the books with no missing pieces, and missing pieces including text or not. Left: C collection. Right: NC collection.

Only about 2.6% of the books of the NC collection has missing pieces with text, which could affect the fitness for use, whereas the proportion (about 13.1%) is notably higher in the C collection. However, the objects of the C collection are documents to which a particular cultural value has been associated, so that missing pieces containing text have little impact on fitness for use.

The percentages of books with tears in the C and NC collections (about 41% and 20%, respectively) are higher than those of books with missing pieces (about 23% and 16%, respectively). These results are in line with those reported by Strlič and co-authors [93] according to which missing pieces accumulate more slowly than tears, missing pieces developing as a function of tears.

As far as the different types of ink are concerned, firstly, ink was classified as iron gall ink (brown, typically used for manuscripts), coloured ink for manuscript, and printing ink (typically black). When more than one ink was present, the book was classified as multiple inks. Indeed, on the basis of what was found on Italian manuscripts dated between the 14th and 16th century [101], it is reasonable to classify the brown ink found in the manuscripts analysed in the present survey as iron gall ink, the typical writing ink used from the medieval time to the first half of the 20th century. While, carbon black ink, largely more stable than iron gall ink, is likely to be the ink used in the printed documents, i.e., incunabula and printed books of the NC collection in the present survey.

Figure 3.32 shows that the C collection is characterised by books with different kinds of ink, about a half, while nearly all the books of the NC collection have only printing ink.

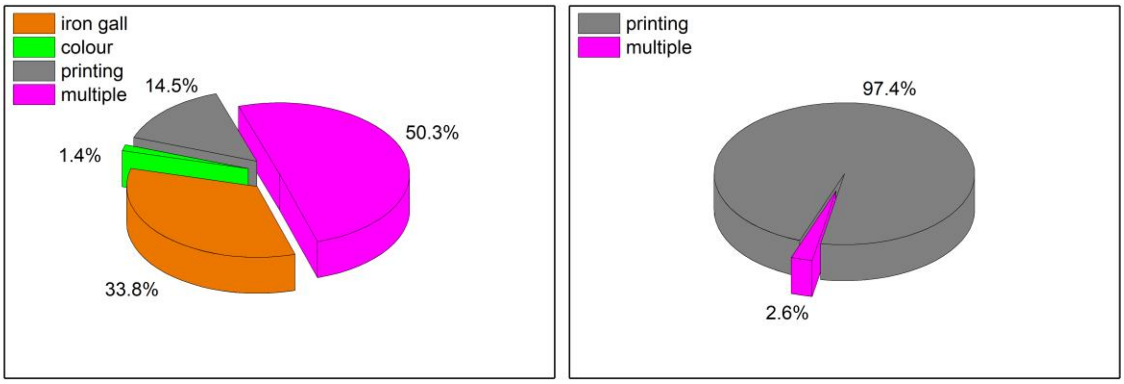

Figure 3.32. Percentages of the books with different kinds of ink.

The high proportion of books of the C collection with multiple inks can be accounted for the 30 incunabula that have manuscript notes throughout the text, along the borders of the pages (see Figure 3.20). As a total, 114 items out of 145 objects analysed in the C collection have manuscript inks.

Damages due to the ink transfer through the page was assessed on a four-level scale of ink transfer, the 4th being the most damaged (see Figures 3.13, 3.14 and 3.17). The results indicate that most of the analysed items fall in the 1st and 2nd level for all kinds of ink. However, whereas in both collections printing inks were not associated with the 3rd and 4th levels of degradation, about 40 samples of the C collection with manuscript ink fall in the 3rd and 4th degradation range, confirming that this kind of ink has degradative effects on paper, as reported elsewhere [39–41]. Figure 3.33 displays the number of books of the

C collection with iron gall ink classified by transfer category in each time interval to examine ink damage over time.

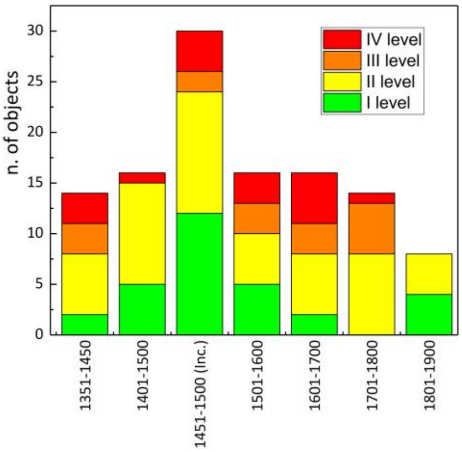

Figure 3.33. Distribution of books of the C collection with manuscript inks, classified as a function of ink corrosion category, over the time.

No clear trend of the ink corrosion categories over the time (see Figure 3.33) emerges. In fact, the time interval 1601-1700 counts 5 and 3 books classified as 4th and 3rd level of ink corrosion, respectively, while the 1401-1500 period has only 1 book classified as 4th level of ink degradation and none as 3rd level.

Finally, Figure 3.34 (left) shows that a considerable number of books of the C collection has clear evidence for previous repairs or replacements of the cover, binding, or spine. On the other hand, Figure 3.34 (right) shows that a relatively small number of books (24%) has been restored in the NC collection.

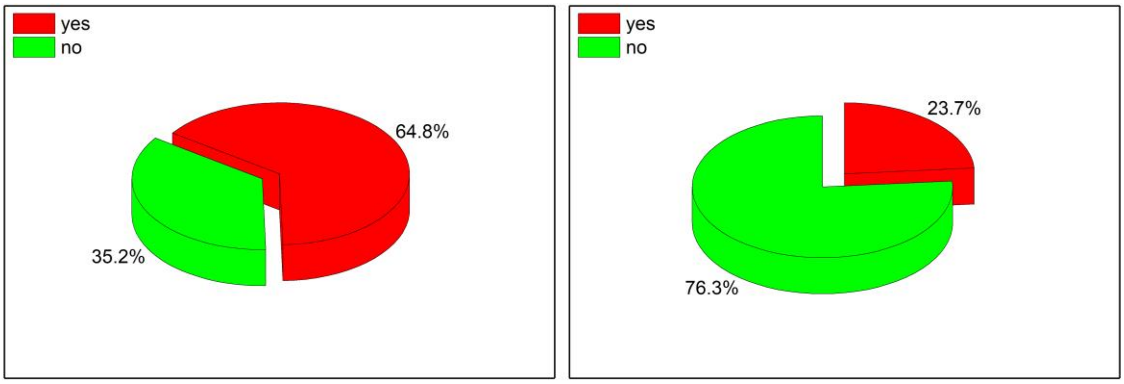

Figure 3.34. Percentages of books with previous repair/replacement of parts of the book.

In both collections the cover is the most frequent restored or replaced part, while page repairs (e.g., with Japanese tissue, see Figure 3.18) occur with a much lower rate. To the best of librarians' knowledge, most of these repairs were made during a huge restoration campaign conducted at the end of the 19th century (1895). Only a few books were restored recently. In this case, the books report a tag of the laboratory where the restoration was carried out (e.g., Biblioteca Apostolica Vaticana) at the endpaper.

3.4.3 Paper characterisation

Although to different extents, the chemical and physical properties measured using the SurveNIR instrument contribute to an overall description of book samples, each property being discussed separately in the following sections. It is worth stressing that the SurveNIR results have to be considered as modelled values, i.e., derived from chemometric models, such as those described by Trafela and co-authors [79] and Lichtblau and co-authors [80] with corresponding associated errors.

3.4.3.1 Paper types identification

Three types of paper, namely, rag, groundwood and bleached pulp paper, were identified by the SurveNIR in the analysed books. In particular, the results indicate that all books of the C collection are made of rag fibres, while the NC collection has also books made of groundwood and bleached pulp paper. Figure 3.35 shows the percentages of the types of paper identified. It is to be noted that the proportions are relative to all the analysed books, as a single whole collection. Therefore, 48.8% of books made of rag fibres in the C collection represent all the 145 books of the C collection, while 33.0% corresponds to 98 items of the NC collection.

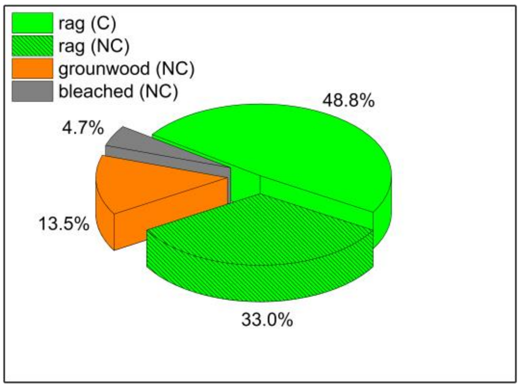

Figure 3.35. Percentages of the various paper types in all the analysed books

Overall, most of the books analysed (about 82%) are made of rag paper, as expected since most of them (about 75%) are dated before 1850. The oldest bleached pulp paper book is dated 1896, while the oldest item identified as made of groundwood paper was initially dated 1834. However, the publication date of this latter item was object of further investigation, given that the diffusion of wood-derived fibres in the papermaking technology is generally dated later [102]. In fact, it turned out that 1834 is the date of publication of the preface, while the rest of the text could have been printed later. It was rather unusual, but possible, that a book included a letter, a dedication or a preface already published in previous editions.

3.4.3.2 Acidity

Acidity is known to play an important role in the rate of paper degradation [1,103,104], as discussed in Chapter 1 and 2. The present results indicate that the pH values of the analysed books cover a wide range, from 2.7 to 8.0. As shown in Figure 3.36 (left), the acidity has significantly increased since the second half of the 20th century, when the introduction of additives and chemical processes in the papermaking extensively affected the pH of the paper. Figure 3.36 (right) shows that about 61% of the analysed books have pH values within 6.0 and 7.0, none of them being made of groundwood paper. This latter type of paper, in fact, as expected, is characterised by very low pH values, ranging from a minimum of 2.7 to a maximum of 4.9. On the other hand, it is interesting to note that the books made of bleached pulp paper have a wider, but on the average less acidic, pH range (3.6 - 6.6). It is also interesting to note that generally rag paper books of the C collection have higher pH values than those of the NC collection.

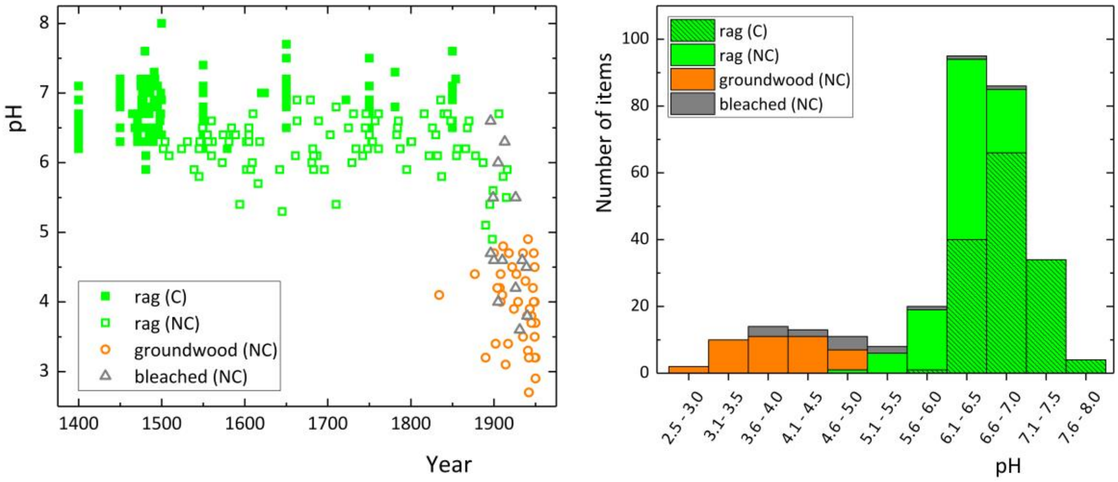

Figure 3.36. pH values. Left: distribution of pH values for all the books analysed as a function of the publication date and paper types. Right: number of items as a function of pH.

3.4.3.3 Degree of polymerisation

Together with pH, DP is a key factor in paper degradation. It is to be noted that the DP values could not be evaluated for groundwood paper books, as the reference method for the estimation of DP implemented on the SurveNIR system is viscometry in CED. This traditional and standardised method [105] is accepted and used for lignin-free paper (i.e., paper with a low lignin content) because lignin can not be completely dissolved in CED. Figure 3.37 (left) shows that the DP values of the books made of wood-free paper go from a minimum of 500 to a maximum of 2600. Unlike pH, no clear trend with publication date and paper type is evident. Figure 3.37 (right) shows that the DP values of about 40% of the books ranges from 1300 to 1600, while about 23% has DP values in the 1700-2000 range.

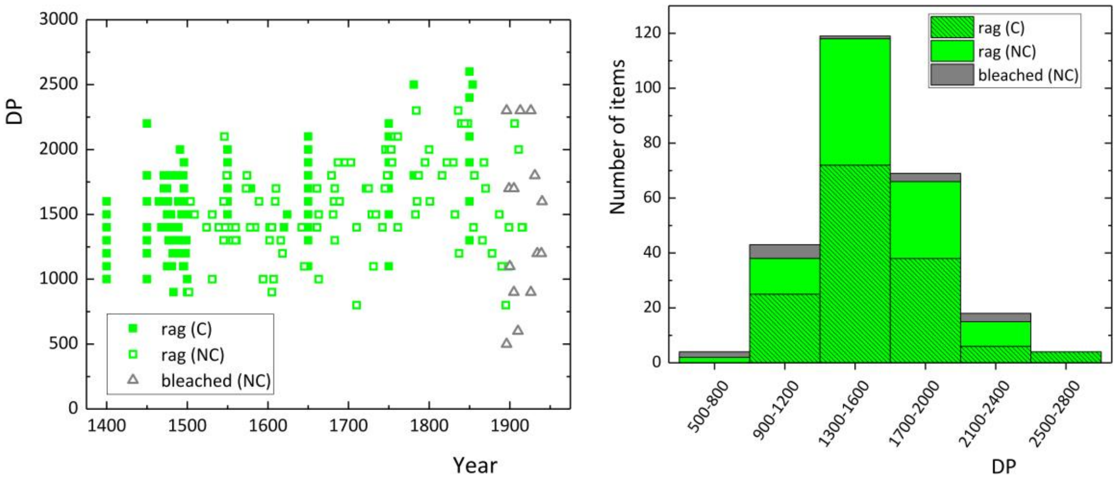

Figure 3.37. DP values. Left: distribution of DP values for all the books analysed as a function of the publication date and paper types. Right: number of items as a function of DP.

3.4.3.4 Tensile strengths

The tensile strength (TS) and tensile strength after folding (TSF) are useful parameters in terms of the paper usability. Although TSF is not a standardised measure, it was chosen as a paper property of interest, together with TS, because it resembles the manual fold test commonly used in condition surveys conducted so far. Both properties are related to the mechanical strength. TS reflects the strength of a sheet of paper not subjected to mechanical stress, while TSF shows the strength after a mechanical stress (folding).

Figure 3.38 (left) shows the TS values measured for all the analysed books, and provides evidence for a decrease of the TS values for groundwood and bleached pulp papers with respect to books made of rag paper. Interestingly, Figure 3.38 (right) indicates that the books made of rag paper have different typical TS values in the two environments considered: about 76% of these books in the C collection have TS values ranging from 51 to 60 N, while in the NC collection about 71% have TS values in the 41-50 N range. Several tentative explanations could be put forward. One of these could stem from the larger temperature and humidity fluctuations present in the rooms that house the NC collection. Such cycling thermo-hygrometric conditions cause creep of paper, possibly associated with physical degradation [12]. However, it is worth precising that even though the thermo-hygrometric conditions have been controlled for only 6 years, the books were placed in the Caveau much earlier. In this way, the books were likely prevented by large seasonal fluctuations typical of the other environments. Another reason could be related to a better paper quality of the books stored in the Caveau.

Moreover, Figure 3.38 shows, at first glance, that groundwood and bleached papers have in general lower TS values than rag paper. In agreement, lignin does not have a negative impact on mechanical properties only if the paper is buffered with a sufficient amount of calcium carbonate [106].

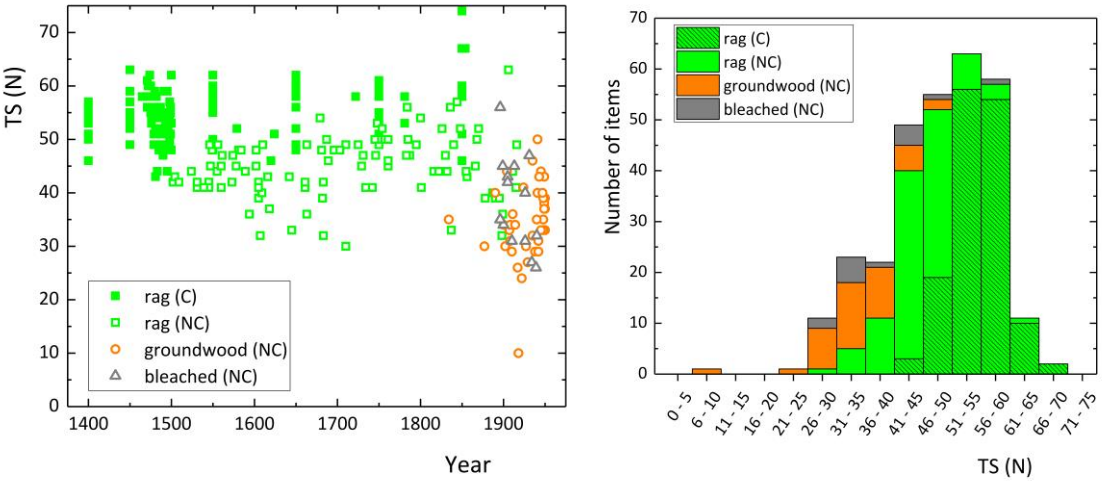

Figure 3.38. TS values. Left: distribution of TS values for all the books analysed as a function of the publication date and paper types. Right: number of items as a function of TS.

As far as TSF is concerned, as mentioned before, it reflects the method traditionally used in library condition surveys to estimate the brittleness of paper. The trend of the TSF values as a function of year of publication, shown in Figure 3.39 (left), parallels the one found for TS, although lower values are more frequent for the NC collection. Figure 3.39 (right) clearly shows a shift toward lower TSF values with respect to TS values, mainly for groundwood papers.

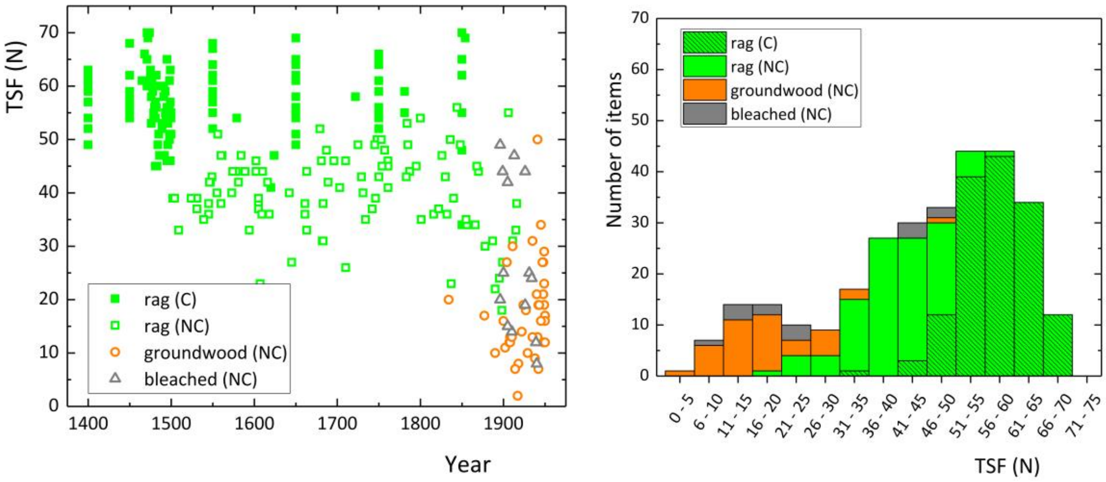

Figure 3.39. TSF values. Left: distribution of TSF values for all the books analysed as a function of the publication date and paper types. Right: number of items as a function of TSF.

It is plausible to consider that the difference between TS and TSF can depend on the extent of degradation of the paper. TSF should reasonably be not much smaller than TS for slightly degraded paper, the difference for degraded paper being generally larger. The reason is that a degraded paper is more prone to break after mechanical stress (i.e., fold). Figure 3.40 shows that for some books TSF is remarkably lower. This indicates that these books, mostly made of groundwood paper and bleached pulp paper, could be more degraded in terms of mechanical properties. In contrast, most of the books analysed have comparable TS and TSF values, suggesting their good condition in terms of mechanical properties. Moreover, it seems that the mechanical properties are not only influenced by the kind of paper, but also by storage environments, all the books with TSF values lower than TS being made of groundwood or bleached pulp paper, and housed in the non-controlled environment in case of rag paper.

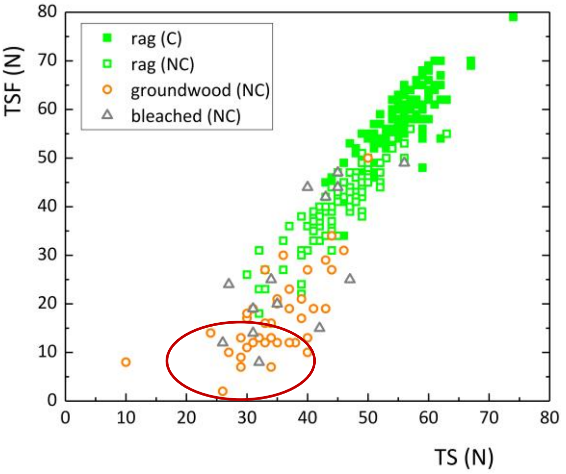

Figure 3.40. Relationship between TS and TSF. The points inside the circle represent books with paper having TSF lower than TS.

For paper-based materials, brittleness is often considered the most important consequence of environmentally induced chemical degradation. Zou and co-authors [107] performed accelerated ageing experiments using paper of pure cellulose and concluded that a decrease of fibre strength, responsible for the loss of mechanical strength and embrittlement, was due to depolymerisation of the cellulose chains caused by acid-catalysed hydrolysis. There have been many attempts to correlate mechanical properties with a more easily measurable quantity. It has been estimated that with a DP of 250, paper becomes too brittle even to be tested for its tensile strength [108]. In another study, it has been found that sixfolds correspond to a DP of approximately 350 [109], although the interpretation of the results requires caution as the uncertainty associated with the manual fold test was found to be significant. Studies of iron gall ink drawings [40] and cellulose-based painting canvases [110] assessed that the risk of damages during handling became too high for DP ≤ 400. A correlation between DP and mechanical properties, such as tensile strength and fold endurance, has been reported in the literature [103]. Strlic and co-authors [93] have recently shown that paper with very low DP values has low fold endurance and tensile strength, and it is experienced by readers as brittle and difficult to handle. The same study [93] demonstrated that an appreciable accumulation of missing pieces, that can be traced back to brittleness, mainly (95-98%) occurred in objects with DP < 300, only 2-5% of all missing pieces deriving from paper with DP > 300. Therefore, it was concluded that the DP value of 300 could be used as a threshold for safe handling, and that the accumulation of wear and tears depends on DP for paper with DP < 800, while for paper with higher DP, mechanical deterioration appears to accumulate at a very low rate, randomly and independently of DP [93]. The DP values measured in this survey are > 800 expect for 4 books. For this reason, the correlation found between handling and missing pieces [93], has not been considered here. The influence of handling on missing pieces, in fact, is believed to occur only for DP ≤ 800. In agreement, Figure 3.41 shows that there is little correlation between DP and TS.

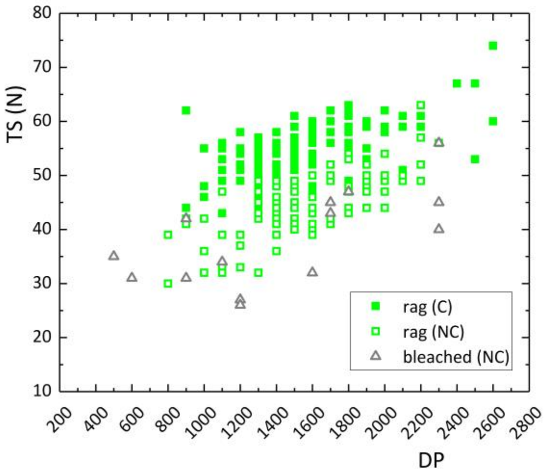

Figure 3.41. TS as a function of DP for all the analysed books.

3.4.3.5 Lignin content

The amounts of lignin in different kinds of paper can vary considerably. Although this polymer is characteristic of wood fibres, also rag paper can contain small amounts of lignin. Papers originated from wood fibres can have a considerably different lignin content. In fact, bleached pulp and groundwood papers are both based on wood-derived fibres, but the amount of lignin in bleached pulp is significantly reduced by chemical processes (e.g., treatments with soda, sulphate, sulphite), whereas groundwood paper, mechanically produced, has a high amount of lignin. Unlike in plants, lignin in paper does not provide mechanical stability. Its influence on paper degradation is not completely understood yet. Its limited photostability causes yellowing of the paper upon oxidation, oxidation itself can contribute to accumulation of acids, thus destabilising the material, as outlined in Chapter 1. However, lignin seems also to act as a radical scavenger, providing an antioxidant effect [111].

Figure 3.42 (left) displays the lignin content in all the analysed books, as a function of publication date, confirming that the use of wood-derived fibres in the papermaking technology around the second half of the 19th century has determined a significant increase in lignin content. Figure 3.42 (right) shows that a very low proportion of books has a high lignin content: only 15% of all measured books (C + NC collections) has a lignin content > 50 mg/g. The lignin content of the books made of rag paper is typically below 25 mg/g, while for the books made of groundwood paper the lignin content ranges between 73 and 303 mg/g.

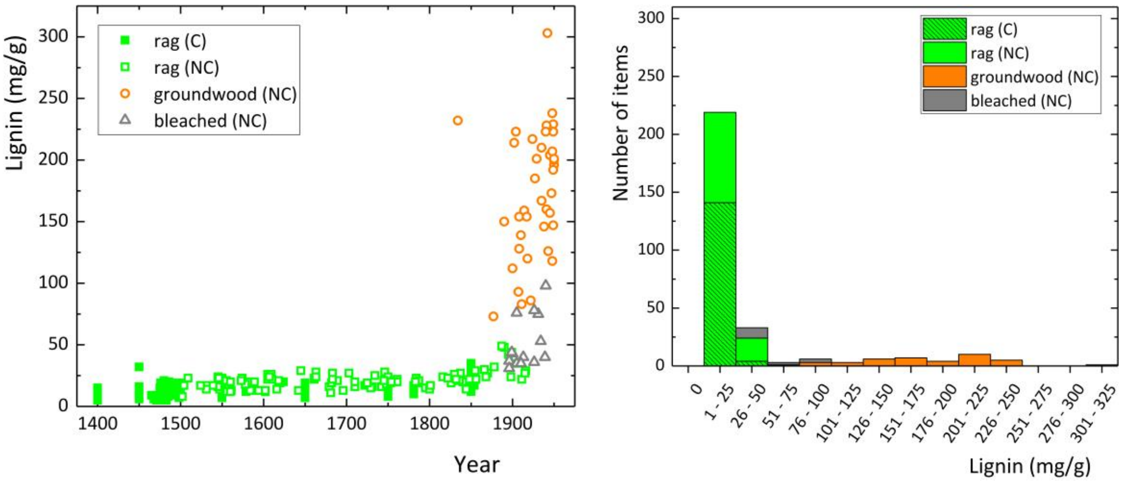

Figure 3.42. Lignin contents. Left: distribution of lignin contents for all the books analysed as a function of the publication date and paper types. Right: number of items as a function of lignin content.

Moreover, as expected, the books made of bleached pulp papers have less lignin than those made of groundwood paper. Figure 3.43 shows that the lignin contents found in the bleached pulp paper books range from 31 mg/g to 98 mg/g.

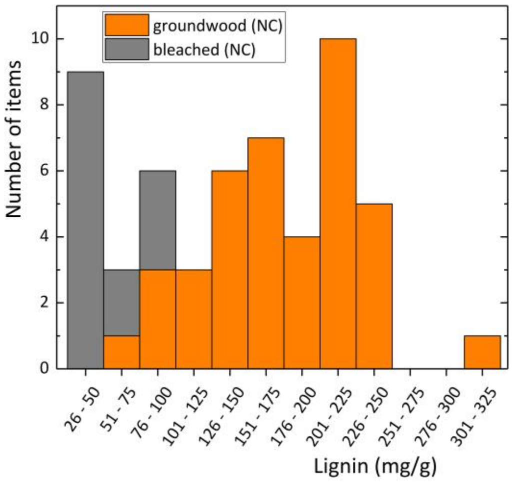

Figure 3.43. Number of books made of bleached pulp and groundwood paper as a function of lignin content.

3.4.3.6 Rosin content

In 1807, Moritz Friedrich Illig publicised his invention of alum-rosin sizing in Germany [102]. From the mid-19th until the final decades of 20th century, rosin was added to the pulp and precipitated with aluminium salts to size the paper internally during the papermaking process at acidic pH values, usually between 4 and 5. Such a low pH was required to allow the aluminium(III) cations to form bonds between rosin and cellulose fibres. The presence of these aluminium ions, however, was found to increase the paper degradation rates [112]. Alum, used in concentrations as high as 20%, stabilized the viscosity of the size and reduced biodeterioration [1], as outlined in Chapter 1.

Figure 3.44 (left) displays the increase of rosin content in the books printed after 1800, as expected, although some outlier values can be detected.

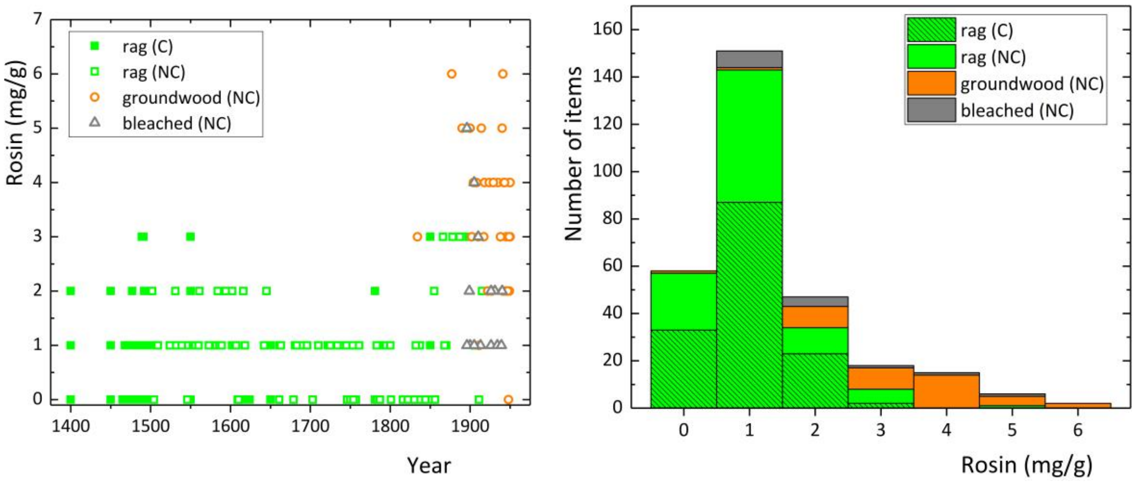

Figure 3.44. Aluminium contents. Left: distribution of aluminium contents for all the books analysed as a function of the publication date and paper types. Right: number of items as a function of aluminium content.

3.4.3.7 Protein content

Starch and flour were the early materials commonly used for internal sizing. Since the 13th century, gelatine derived from collagen, the connective tissue in skin, cartilage, sinews and ossein of animals, had been used as surface sizing in Europe and continuously thereafter, becoming the most common surface sizing before Mortiz Illig's invention of rosin-alum sizing. From the 17th century on, gelatine was frequently used in concert with additives, especially alum, occasionally replaced by zinc sulphate (white vitriol) [1]. It has been demonstrated that gelatine can act as a pH and moisture content buffer [113].

The results of the present survey indicate a decreasing protein content with the publication date, higher percentages of protein being measured in historical books made of rag paper. Interestingly, Figure 3.45 (left) shows that very low protein contents (0-1%) are measured for the books dated after 1807, when the gelatine sizing was replaced by the alum-rosin sizing, as mentioned above. Figure 3.45 (right) displays that the books with paper made of rag fibres have a wide protein content range, from 0 to 7.4 %, while the books with groundwood and bleached pulp paper have smaller protein contents (< 1.6%).

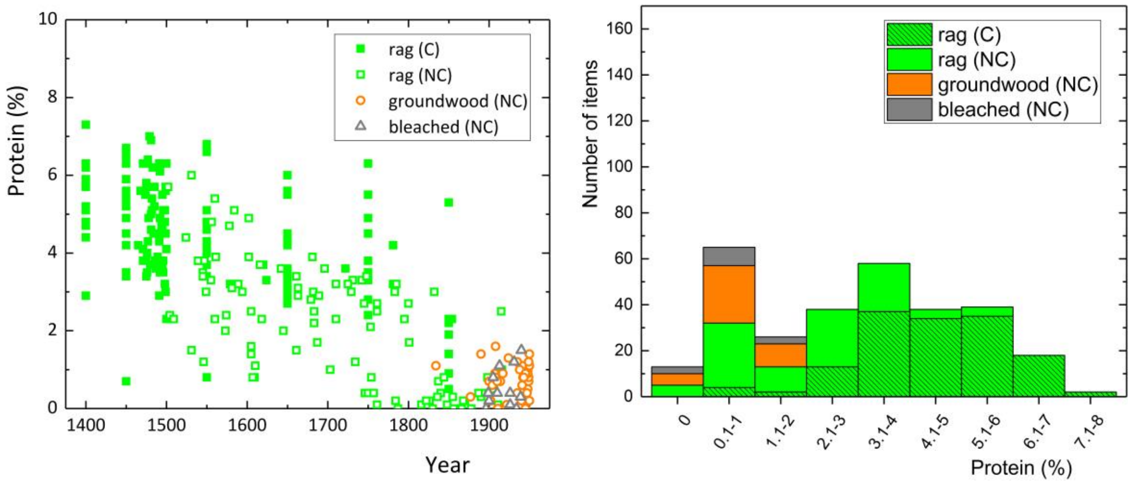

Figure 3.45. Protein contents. Left: distribution of protein contents for all the books analysed as a function of the publication date and paper types. Right: number of items as a function of protein content.

Generally, the books of the C collection have higher contents of gelatine than those of the NC collection. In this regard, it is worth noting that gelatine-sized papers were found to age more slowly than non-sized papers [114,115]. Stephens and co-authors [116] concluded that papers with high gelatine contents were in good condition, while low gelatine paper samples ranged from poor to good condition. Overall, these results are in line with the general conclusion for which papermakers used less gelatine over the course of the centuries [10].

3.4.3.8 Optical brighteners

No evidence of optical brighteners was found in all analysed books, although fluorescent whitening agents were tested for the first time in 1936 [102].

3.4.3.9 Kaolin, talcum and gypsum

As far as the fillers added as paper components are concerned, kaolin, talcum, and gypsum were qualitatively measured by SurveNIR. It turned out that only two books of the C collection, hence made of rag paper, were evaluated to have some kaolin, but no talcum and gypsum were detected in the books of the C collection. For the NC collection the results are reported in Table 3.5.

Table 3.5. Number of books of the NC collection which contain kaolin, talcum or gypsum.

	Kaolin		**Talcum**		**Gypsum**	
	Yes	Not	Yes	Not	Yes	Not
Rag paper	9	89	3	95	0	98
Groundwood paper	26	14	10	30	1	39
Bleached pulp paper	10	4	4	10	0	14

It is to be noted that all books that contain kaolin are dated after 1780, when clay loadings became of general use [102].

3.4.3.10 Statistical analysis

The existence of correlations between variables measured by the SurveNIR was statistically investigated. Figure 3.46 shows the matrix correlation between each pair of quantitative variables. As expected, pH is inversely related to lignin and rosin, while positive correlations between pH and mechanical properties (TS and TSF) are found, indicating that the less acidic the paper, the less fragile it is. Poor correlations emerge between DP and other variables, including pH. However, it is to be noted that the dataset does not include DP values for groundwood paper, characterised by low pH values.

As far as the correlation between pH and rosin is concerned, it turns out that it is higher than that found for pH and protein, contrary to what concluded by Barrett and co-authors [10].

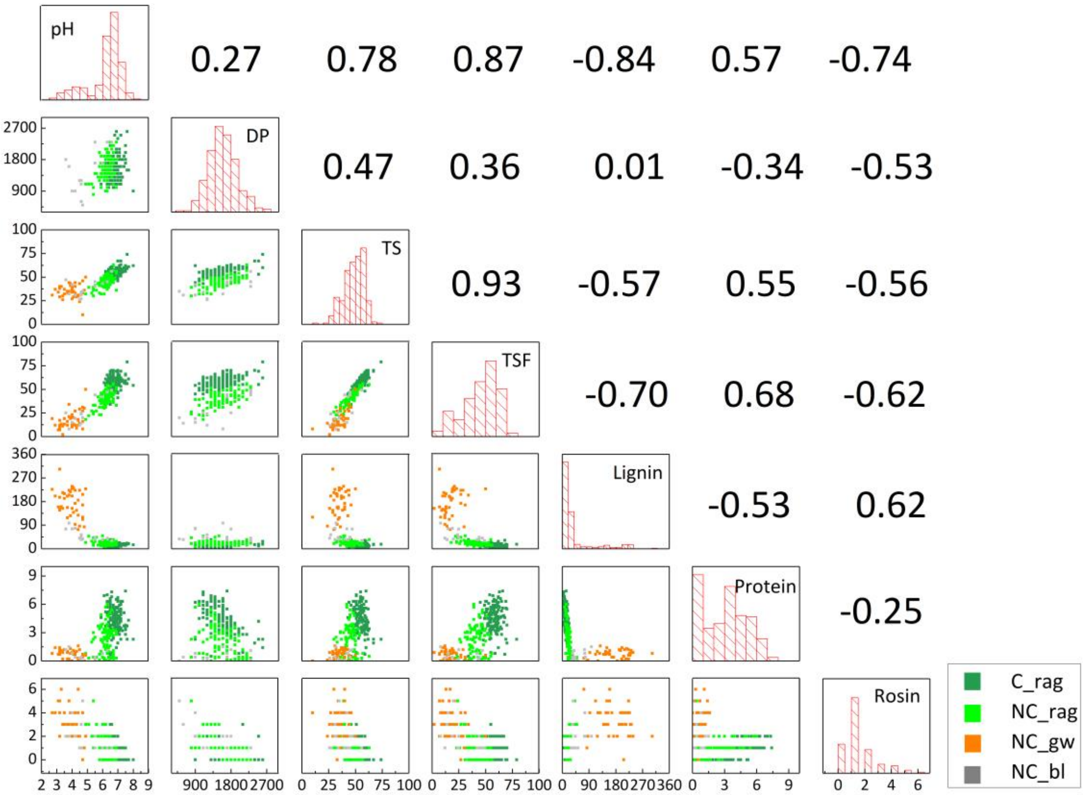

Figure 3.46. Correlation matrix of each pair of quantitative variables. The lower triangle displays pairwise scatter plots, in which the colours represent different pulps and storage environments. The diagonal reports frequency histograms. The upper triangle displays pairwise correlation coefficients.

According to principal component analysis (PCA) [88–90], the first two principal components account for about 85% of the cumulative variance. Figure 3.47 shows the resulting biplot in which the observations and positions of the considered variables are displayed in the new two-dimensional space.

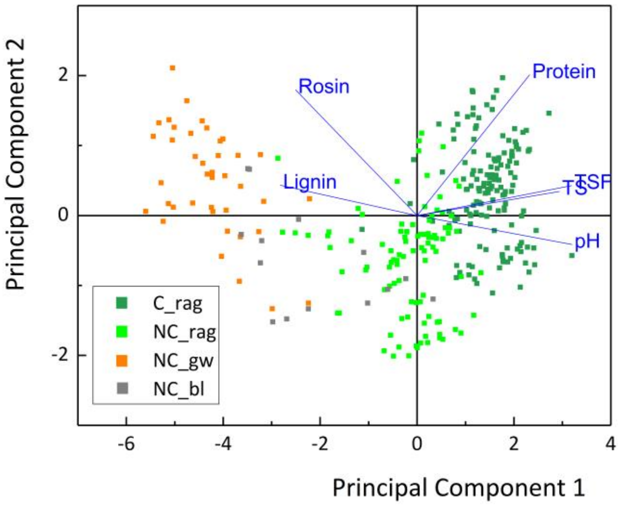

Figure 3.47. Biplot obtained from the PCA. The colours of the observations represent different pulps and storage environments.

The vectors corresponding to TS and TSF are close to each other, indicating their large positive correlation, as also pointed out by the correlation matrix. Lignin and rosin are located in the quadrant opposite to that of pH, confirming their negative correlation with the latter. Furthermore, it can be noted that the main contributions to the first component, which accounts for approx. 72% of variance, come from pH, TS, TSF and lignin, while protein and rosin load mainly the second component. Figure 3.47 also shows that the first two principal components distinguish satisfactorily different pulps, separating fairly well the rag paper from the groundwood and bleached pulp paper. In addition, the rag paper books stored in the Caveau are also separated from those housed in the non-controlled environments. A significant contribution to this distinction could be traced back to the larger protein content in the more ancient and better-quality books stored in the Caveau, as suggested by the protein vector (see Figure 3.47).

To verify the results supplied by PCA, a multivariate analysis of variance (MANOVA) using the Wilks' lambda test [91] was performed. The storage environments along with the three types of paper identified by the SurveNIR were used to group the books in four categories: rag paper books stored in the Caveau (C_rag), rag (NC_rag), groundwood (NC_gw), and bleached (NC_bl) paper books stored in the non-controlled environments. In particular, two MANOVA analyses were carried out at the $\alpha=0.01$ significance level: the first one compares the rag paper books housed in the two environments (i.e., C_rag vs NC_rag), the second one compares groundwood and bleached paper books (i.e., NC_gw vs NC_bl). MANOVA indicated that there is a significant difference between the two groups of rag paper (Wilks' lambda=0.30, $F_{7,233}=2.72$). Significant differences are found for all variables, except for DP and rosin. Indeed, these results are in line with the intervals of confidence for the means reported in Table 3.6. The differences relative to the mechanical properties and protein content could be associated with the different grade of paper stored in the two environments and different median ages of the books of the two groups, respectively, as mentioned in the previous section. Comparison between groundwood and bleached paper books (i.e., NC_gw vs NC_bl) indicates that these two groups are also significantly different (Wilks' lambda=0.31, $F_{6,47}=3.21$). However, the differences in terms of TS and protein content are not statistically significant, as also indicated by the intervals of confidence of the means (see Table 3.6).

Table 3.6. Means and intervals of confidence at P=0.95 for all the measured variables of the four different groups (C_rag, NC_rag, NC_gw, and NC_bl referring to rag paper books stored in the Caveau, rag, groundwood, and bleached pulp paper books stored in the non-controlled environment, respectively).

	pH	**DP**	**TS (N)**	**TSF (N)**	**Lignin (mg/m)**	**Protein (%)**	**Rosin (mg/g)**
C_rag	6.82±0.06	1548±55	55.0±0.8	57.6±1.0	12.9±0.9	4.5±0.2	0.96±0.11
NC_rag	6.22±0.08	1559±70	44.8±1.2	40.1±1.5	21.5±1.4	2.1±0.3	1.03±0.18
NC_gw	3.92±0.18	Na	34.8±2.3	17.7±2.9	174.9±16.3	0.7±0.1	3.35±0.41
NC_bl	4.89±0.54	1436±355	38.1±5.0	27.7±8.3	51.5±12.2	0.5±0.3	1.93±0.73

3.4.4 Environmental scenario modelling

Considerations about collections lifetime and usability were derived by further elaboration of the measured DP and pH values, although these predictions are inevitably affected by some uncertainties. Combining such properties (pH and DP) with a dose-response function, recently modelled [94], and a wear-out function [93], the effects of the storage environments (T and RH) on the collections analysed were estimated through isochrones and demography graphs.

3.4.4.1 C collection

The C collection groups the books housed in the Caveau, the controlled environment room of the Classense Library. To calculate the isochrones, firstly, the C collection was subdivided into pH groups, as reported in Table 3.7.

Table 3.7. Sets of books of the C collection grouped by pH. The first and the last groups have a larger pH range because only one book has pH 5.9 and only one has pH 8.0.

pH groups	**pH interval**	**% of C collection**	**pH average**	**DP_0 average**
1st group	5.9 – 6.4	14	6.3	1400
2nd group	6.5 – 6.9	50	6.7	1557
3rd group	7.0 – 7.4	30	7.1	1560
4th group	7.5 – 8.0	6	7.6	1767

To describe the C collection in terms of isochrones, the following averaged values were used:

- average pH = 6.3 – average DP_0 = 1400 → 14% of the C collection
- average pH = 6.7 – average DP_0 = 1557 → 50% of the C collection
- average pH = 7.1 – average DP_0 = 1560 → 30% of the C collection
- average pH = 7.6 – average DP_0 = 1767 → 6% of the C collection

Figures 3.48-3.51 show the isochrone plots of the groups of the C collection.

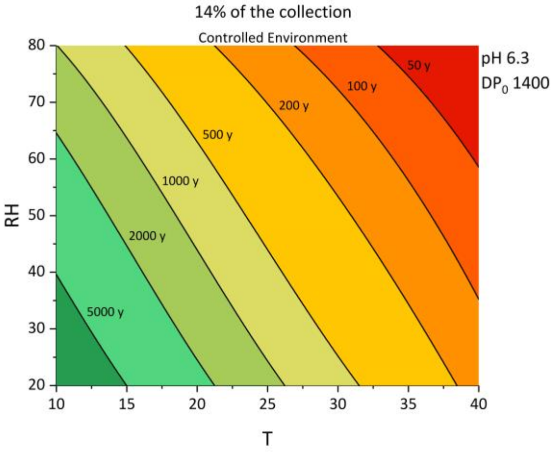

Figure 3.48. Isochrones for the books of the C collection with average pH=6.3 and DP$_0$*=1400.*

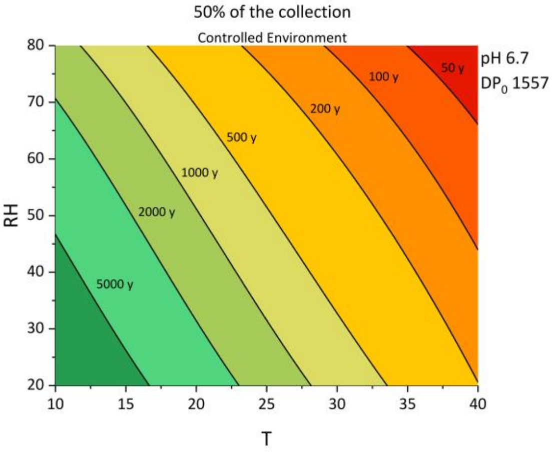

Figure 3.49. Isochrones for the books of the C collection with average pH=6.7 and DP$_0$*=1557.*

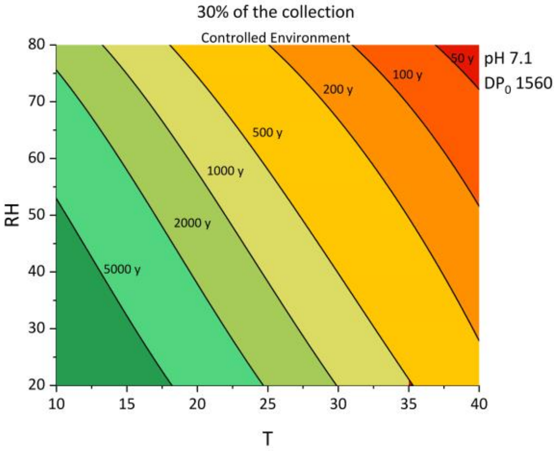

Figure 3.50. Isochrones for the books of the C collection with average pH=7.1 and DP$_0$*=1560.*

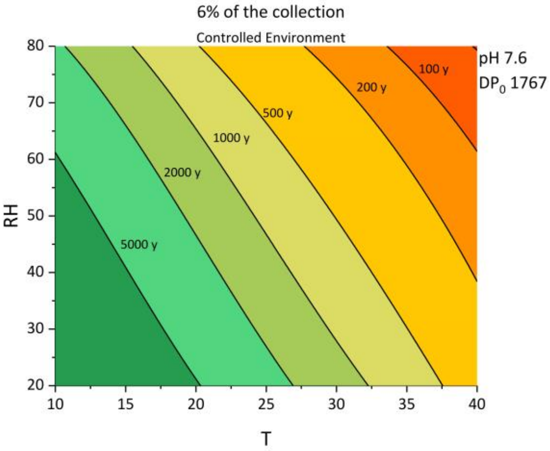

Figure 3.51. Isochrones for the books of the C collection with average pH=7.6 and DP$_0$*=1767).*

As expected, the red/yellow areas are notably reduced with increasing pH, the red one completely disappearing in the least acidic group (see Figure 3.51). It can be appreciated that even the most acidic group of the C collection is predicted to satisfy the long-term planning horizon of 500 years when stored at T=20 °C and RH=60%, namely, the thermo-hygrometric conditions measured in the Caveau.

The demography of this collection was calculated using the constant environmental parameters measured in that room. Figure 3.52 shows the demography plots of the C collection as a whole (left), and grouped by publication date (right).

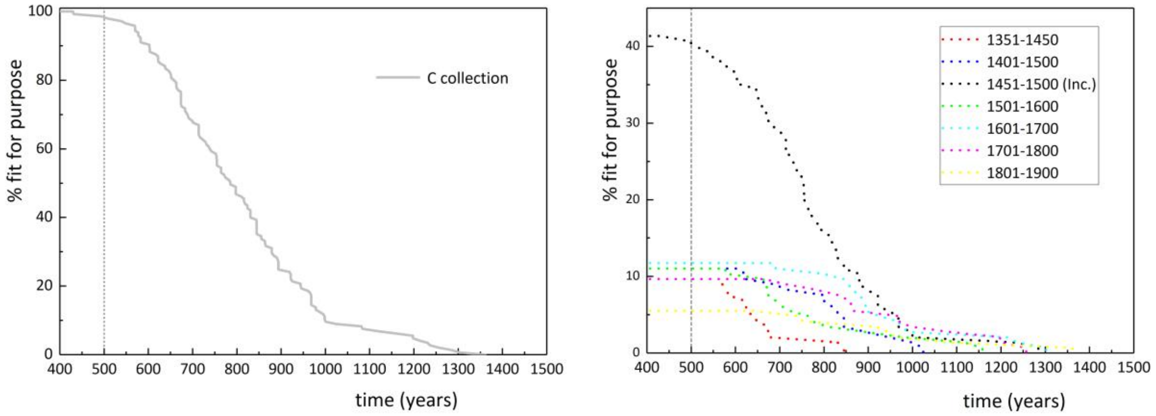

Figure 3.52. Demography of the C collection stored at 20 °C and 60% RH. Left: as a whole. Right: subdivided by strata.

It can be noted that nearly all the books are predicted to survive the long-term planning horizon of 500 years, in agreement with the isochrones (see Figures 3.48-3.51). About 60% of the C collection may be safely handled for about 800 years at these thermo-hygrometric conditions. It is also worth noting that the time required to become completely unfit for use (i.e., intersections of the various curves with the x axis) increases with increasing publication date, as shown in Figure 3.52 (right).

Figure 3.53 confirms the above results showing that the median time for the groups of documents to become unfit increases with decreasing age.

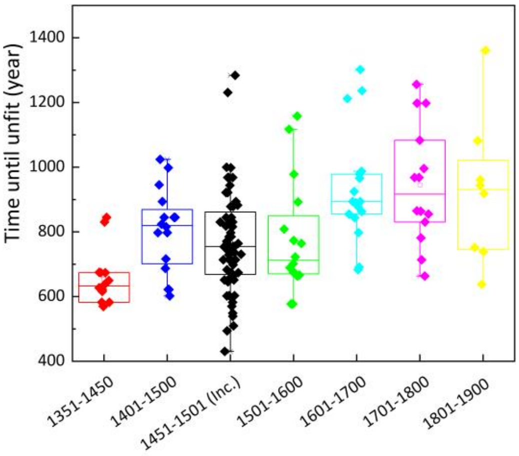

Figure 3.53. Box plots of the predicted times to become unfit for the books of the C collection grouped by strata (20 °C, 60% RH).

Furthermore, it is to be considered that the C collection consists of manuscripts, except for incunabula. 114 items out of 145 have manuscript inks, including notes on incunabula. Therefore, given that iron gall ink, which can be reasonably the ink of the manuscripts analysed, has degrading effects on paper supports, it is necessary to account for its adverse effects on paper stability. Figure 3.54 shows the isochrones calculated considering the books with manuscript inks as paper having pH = 5 and DP = 600, as suggested by Strlič and co-authors [94].

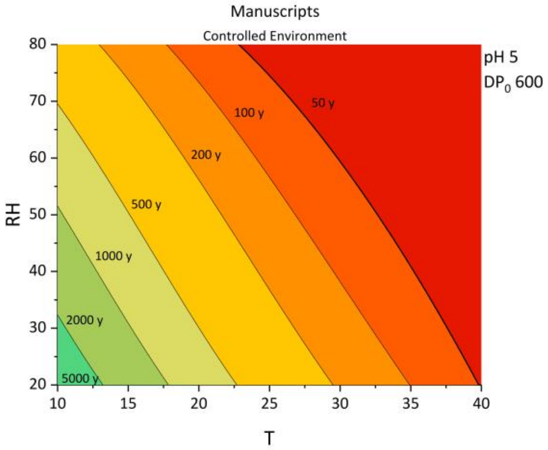

Figure 3.54. Isochrones for the books of the C collection with manuscript ink, assuming pH=5 and DP_0=600.

It is evident that the situation critically gets worse, the intersection between 20 °C and 60% RH being close the 200-year isochrone line. Cooling at T lower than 15 °C should be necessary at 60 % RH, but then problems related to acclimatisation would arise. In fact, not only the books should acclimatise to the new conditions, but it should be considered that the conditions of the storage environment are likely to be different from those of the consultation/reading environment. This has to be considered along with the necessity of involving strategies less energy consuming in view of preventive conservation, as suggested by recent standards [16,25,26].

Additionally, as far as the degradation due to iron gall ink is concerned, Liu and co-authors [42] report that a 1.59 acceleration factor differentiate the rate constants of paper impregnated with iron gall ink from that not impregnated. Figure 3.55 displays the demography plots of the C collection multiplying by 1.59 times the rate constants of items with manuscript ink.

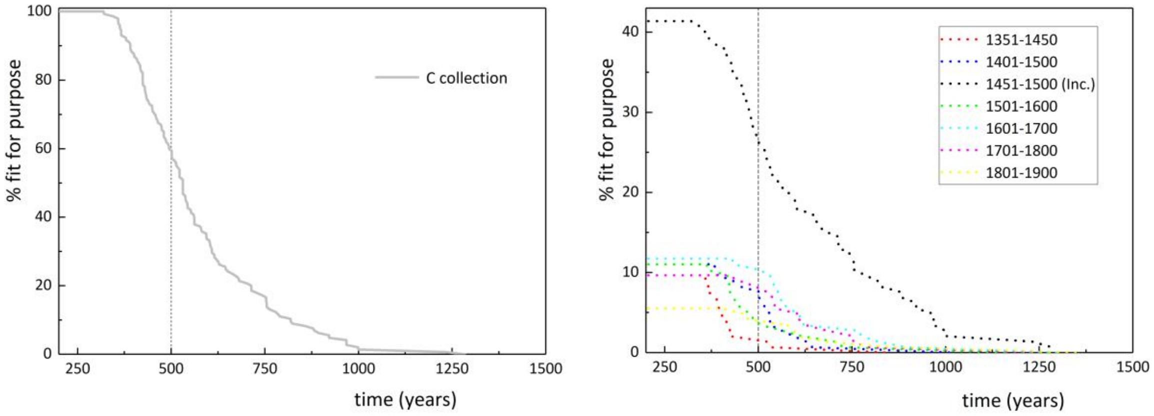

Figure 3.55. Demography of the C collection with the multiplied rate constants for the 114 books with manuscript ink, stored at 20 °C and 60% RH. Left: as a whole. Right: subdivided by strata.

It is evident that about 60% of the books of the C collection is predicted to be in a fit for use state for more than 500 years. This proportion, although smaller than that found without considering the effects of iron gall inks, is promising when compared to the prediction obtained with the elaboration of isochrones for the manuscripts, assuming pH 5 (see Figure 3.54).

3.4.4.2 NC collection

As done for the books housed in the controlled environment, the NC collection was subdivided into pH groups, as reported in Table 3.8. It is to be noted that in both collections each group spans 0.5 pH units, except for two intervals of the C collection slightly smaller (0.4, see Table 3.7), and one of the NC collection slightly larger (0.6, see Table 3.8).

Table 3.8. Sets of books of the NC collection grouped by pH. The last group is larger because only three books have pH 6.9. The asterisks indicate the groups of books made mainly of groundwood paper, for which DP values are missing.

pH groups	pH interval	% on whole collection	pH average	DP_0 average
1st group	2.7 – 3.2	5	3.1	na*
2nd group	3.3 – 3.8	8	3.6	1700*
3rd group	3.9 – 4.4	11	4.1	900*
4th group	4.5 – 5.0	9	4.7	950
5th group	5.1 – 5.6	6	5.4	1289
6th group	5.7 – 6.2	26	6.0	1528
7th group	6.3 – 6.9	35	6.5	1685

The first three groups of Table 3.8 were not taken into account for the elaboration of isochrones, as most of the books of these groups are made of groundwood paper, their DP values being thus missing. The isochrones and demographic curves were therefore evaluated only for the groups 4-7, which include 9%, 6%, 26% and 35% of the collection, respectively. To describe the groups 4-7 (about 76% of the whole collection), the following average values were used:

- average pH = 4.7 – average DP_0 = 950 → 9% of the NC collection
- average pH = 5.4 – average DP_0 = 1289 → 6% of the NC collection
- average pH = 6.0 – average DP_0 = 1528 → 26% of the NC collection
- average pH = 6.5 – average DP_0 = 1685 → 35% of the NC collection

Figures 3.56-3.59 show the isochrones evaluated for the groups 4-7 of the NC collection.

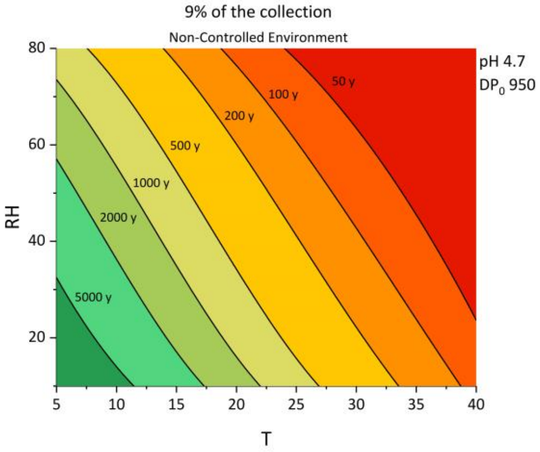

Figure 3.56. Isochrones for the books of the NC collection with average pH=4.7 and DP_0=950.

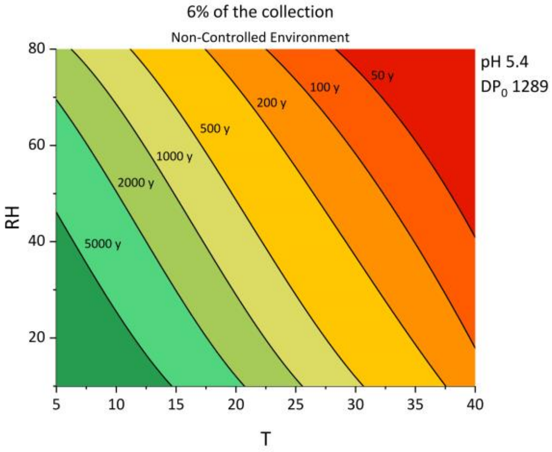

Figure 3.57. Isochrones for the books of the NC collection with average pH=5.4 and DP_0=1289.

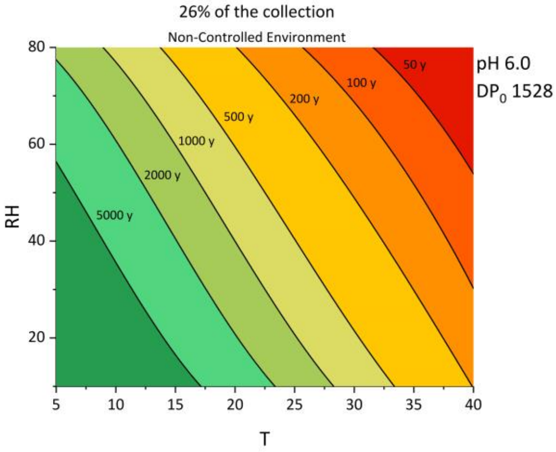

Figure 3.58. Isochrones for the books of the NC collection with average pH=6.0 and DP_0=1528.

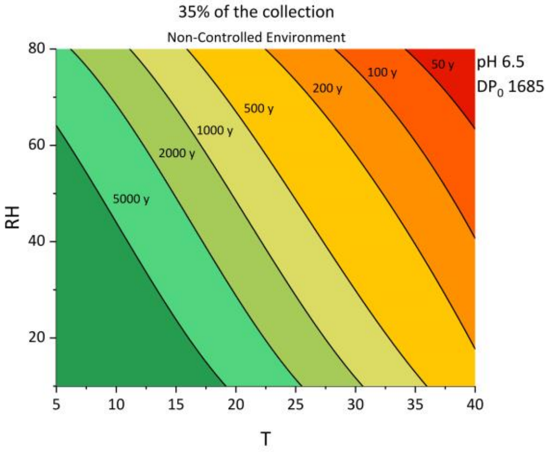

Figure 3.59. Isochrones for the books of the NC collection with average pH=6.5 and DP_0=1685.

It can be noted that only the two most acidic groups (9% and 6% of the NC collection) may not survive the long-term planning horizon of 500 years even if stored at T=20 °C and RH=60 %. Therefore, a reasonable, although qualitative, prediction is that the lifetime of the groups 1-3 (about 24% of the NC collection), because of their lower pH, should be even shorter.

The non-controlled environments, in which the books of the NC collection are housed, are affected by a considerable seasonal trend (see Table 3.1), with temperature variations of 14 °C between winter and summer. The evaluations of the time to become unfit and demographic plots were carried out using three sets of T and RH values, i.e., those measured in summer, winter and in the Caveau.

The left side panel of Figure 3.60 shows the demography plots for the books of the NC collection as a whole (except for the groundwood paper books), while the right side panel displays the books grouped by publication dates, considering the summer environmental conditions (T=27 °C, RH=56%).

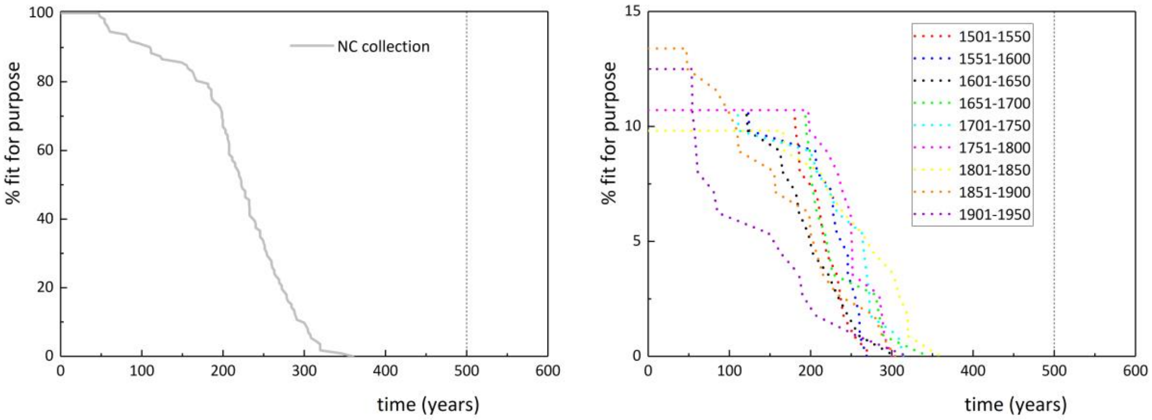

Figure 3.60. Demography of the NC collection stored at 27 °C and 56% RH. Left: as a whole. Right: subdivided by strata.

It can be noted that the predictions of the time to become unfit for use for the documents of the NC collection, considering their chemical properties and assuming that the measured summer thermo-hygrometric conditions occur throughout the year, are not favourable, as expected. No book is predicted to survive the long-term planning horizon of 500 years, about 50% of the NC collection remaining in a fit-for-use state for only 220 years. As expected, Figure 3.61 shows that, in contrast to the trend found in the C collection, the most recent documents (dated between 1851 and 1950) are predicted to have a shorter lifetime than those dated prior to 1851.

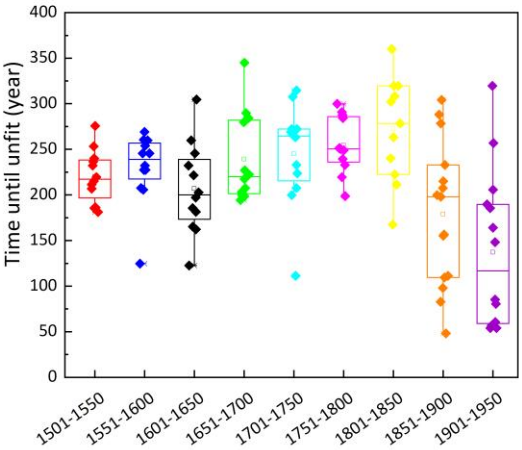

Figure 3.61. Box plots of the predicted times to become unfit for the books of the NC collection grouped by strata (27 °C, 56% RH).

As far as the environmental scenario modelling is concerned, it is to be considered that the contribution of 10 ppb NO_2 to the rate of DP loss was found to be comparable to that of a 4 °C temperature increase, for acidic and rag paper [31,94]. This would lead to an increase of the degradation rate by a factor 1.3. However, less than 5 ppb during summer in the non-controlled environments were measured, and even less in winter time and in the Caveau.

The left side panel of Figure 3.62 shows the demography plots for the books of the NC collection as a whole (except for the groundwood paper books), While the right side panel displays the books grouped by publication date, considering the winter environmental scenario (T=13 °C, RH=65%).

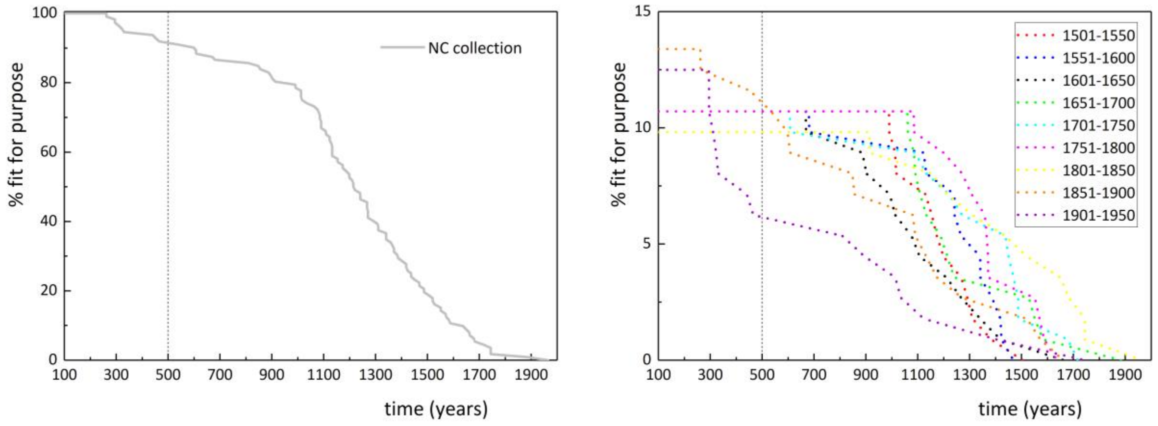

Figure 3.62. Demography of the NC collection stored at 13 °C and 65% RH. Left: as a whole. Right: subdivided by strata.

It is evident that the thermo-hygrometric parameters measured during the winter monitoring campaigns lead to conditions of preventive conservation. The scenario is greatly improved relative to the summer scenario. About 90% of the books of the NC collection are predicted to survive the 500-year horizon. Figures 3.62 (left) and 3.63 show more clearly that only some books dated between 1851 and 1950 are predicted to survive less than 500 years.

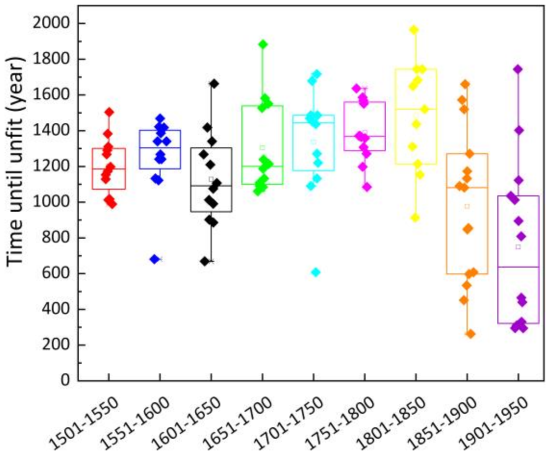

Figure 3.63. Box plots of the predicted times to become unfit for the books of the NC collection grouped by strata (13 °C, 65% RH).

For an average environmental scenario, the T and RH values measured in Caveau (i.e., T=20 °C, RH=60%, see Table 3.1) were chosen. Therefore, these results can indicate the effects of a possible re-shelving of the NC books (or part of them) in the Caveau on the time required to become unfit for use.

The left side panel of Figure 3.64 shows the demography plots of the NC collection as a whole (except for the groundwood paper books), while the right side panel displays the books grouped by publication date, assuming T=20 °C and RH=60%.

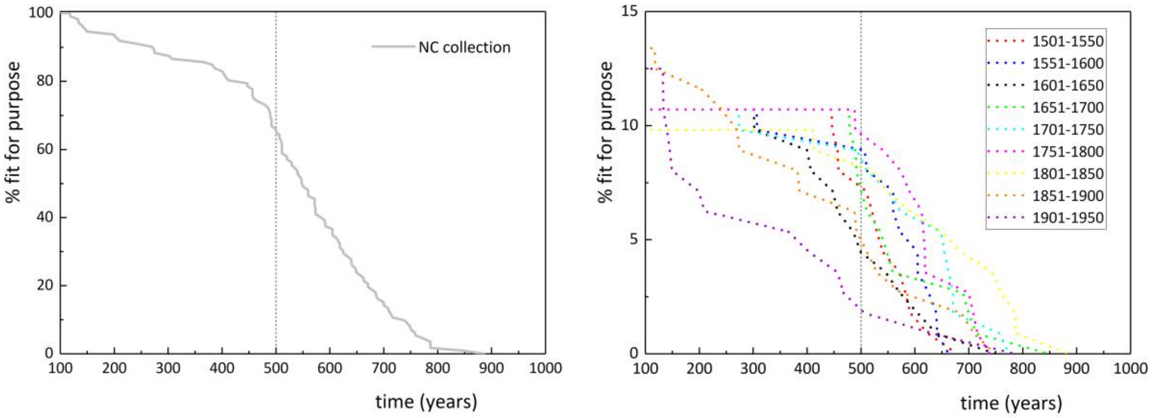

Figure 3.64. Demography of the NC collection stored at 20 °C and 60% RH. Left: as a whole. Right: subdivided by strata.

This scenario predicts that about 65% of the books of the NC collection would survive the long-term planning horizon. However, Figure 3.65 shows that nearly all the books dated 1901-1950 are predicted to be significantly compromised if stored in these environmental conditions by 500 years.

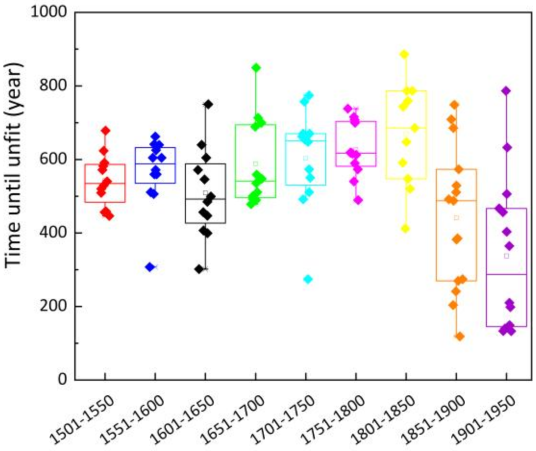

Figure 3.65. Box plots of the predicted times to become unfit for the books of the NC collection grouped by strata (20 °C, 60% RH).

3.5 Conclusions

The present innovative survey investigates the chemical and physical properties along with visually assessed damages of the book collections housed at the Classense, an historical Italian library. About 300 books, including incunabula, manuscripts and modern printed books, dated from the 14th to the 20th century, were analysed in a totally non-destructive and non-invasive way using the SurveNIR system. Two distinct collections were considered: the C collection housed in a controlled environment (Caveau) which groups the most valuable objects; the NC collection housed in non-controlled environments, affected by pronounced seasonal trends. For the first time important chemical and physical paper properties (such as types of pulps, pH, DP, TS, TSF, lignin, protein and rosin contents, presence of optical brighteners) of the collections housed in a historical Italian library were measured.

It is to be highlighted that evaluation of the measured properties derives from the application of chemometric models to NIR spectra, thus being affected by calibration and validation errors. However, the present results allowed, firstly, paper characterisation of the analysed historical Classense collections, and evaluation of their conservation state. Secondly, lifetime predictions were elaborated using the measured pH and DP data in conjunction with recently reported findings on the rate of paper degradation as a function of these parameters.

As far as paper characterisation is concerned, the results are generally consistent with the development and chronology of the papermaking processes, as well as the types of pulps that were identified by the SurveNIR. The pH values show an impressive drop in the books produced between 1850 and 1950. Besides, inspection of possible correlations between pH and other properties unveils largely negative correlations with lignin and rosin. The present survey showed an evident decreasing trend of gelatine content as a function of publication date, in line with literature findings. About rag paper books, the results, especially those relative to pH, gelatine and mechanical properties, suggest that the books stored in the controlled environment are likely made of a better-quality paper or experienced to a lesser extent the adverse effects of thermo-hygrometric fluctuations occurring in the non-controlled environments. In fact, although the controlled environment was implemented only six year ago, the features of the Caveau (such as position, inaccessibility) could have buffered seasonal thermo-hygrometric fluctuations. Statistical analyses (PCA and MANOVA) pointed out that the samples can be grouped on the basis of significant differences in the measured properties and environmental storage conditions. Four groups were identified depending on the types of pulp and storage environments: rag paper books housed in the Caveau, rag, groundwood and bleached paper books housed in the non-controlled environments. A significant contribution to the distinction between rag paper books housed in the controlled environment from those housed in the non-controlled ones, could be traced back to the large difference in the measured protein contents.

As far as the conservation states are concerned, overall, pH and tensile strength values indicate that groundwood paper books are in the worst state. In contrast, rag paper books, especially those stored in the Caveau, resulted to be in the best state of conservation. As far as considerations about the usability in terms of handling/reading are concerned, it is promising that only about 3% of books of the NC collection, to which no particular historical and cultural value has been assigned, has missing pieces including text, that compromise their fitness for use. Although the percentage of books having missing pieces with text of the C collection is higher (about 13%), such a damage, as well as aesthetic damages, should be viewed with more tolerance, as these are books with remarkable historical and cultural value. In this regard, mechanical deterioration (e.g., tears from which missing pieces may derive) seems not to be a concerning issue as DP values were found to be higher that 800 (except for four books).

Further elaborations (isochrones and demography plots) of the measured chemical properties with the support of damage functions, recently modelled for historical paper, allowed to assess preservation scenarios achievable in different environmental storage conditions. The C collection is predicted to be safely read/handled in the long-term planning horizon of 500 years at the thermo-hygrometric conditions of the Caveau. However, the scenarios which account for the effects of manuscript ink predict a worse situation. In this case, in fact, the books are not predicted to be safely read/handled in the 500-year horizon. Therefore, for their preservation, actions, such as treatment with antioxidant and complexing agents, should be evaluated.

The predictions relative to the NC collections are less comforting, as expected. This is due to both the paper properties themselves and thermo-hygrometric conditions of the non-controlled environments. The worst scenario is that elaborated considering the summer environmental conditions, as expected. However, even considering the same conditions of the Caveau, the paper produced after the second half of the 19th century is critically predicted not to be in a fit-for-use state in the long-term planning horizon of 500 years.

Therefore, also in this case, other interventive conservation treatments, such as deacidification, should be considered. Moreover it is to be noted that these scenarios do not take into account the acidic groundwood paper books.

The above findings need to be assessed from a conservation management point of view. For both collections, the next logical step would consist in a cost-benefit analysis. For instance, if the conditions suitable for the desired horizon (e.g., cooling at 15 °C) require continuous financial and energetical investments, a one-off investment as a deacidification treatment should be considered, advantages and drawbacks of both kinds of intervention being evaluated. Moreover, as far as the C collection is concerned, it is to be stressed that the books still maintain a great historical and cultural value even if they can no longer be safely handled.

As a general consideration, such a survey allows to collect a huge quantity of data on paper collections, rapidly and non-destructively, extending its applicability also to collections with historical and cultural worth. Obviously, such a survey can be applied to other libraries and archives, with possible suitable modifications. The interpretation of the present data highlighted the complementarity of visual assessment and NIR measurements. The results of such a survey can provide information, to be combined with a cost-benefit analysis, necessary to address the decision-making process for preservation programs.

3.6 References

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CHAPTER 4

EFFECTS OF γ-IRRADIATION ON PAPER

Abstract

The final Chapter of this doctoral thesis presents a study carried out to investigate the effects of γ-irradiation, as disinfection treatment, on chemical and physical properties of pure cellulose paper. The question about the most effective and appropriate mass disinfection treatment is still debated in the literature, the applicability of γ-rays being especially controversial.

In the present study, samples of pure cellulose paper were irradiated in an industrial apparatus at two doses of γ-rays, 5 and 10 kGy, and were subjected to two additional treatments: thermal drying and ageing (for 24 and 144 h). In this way, with the support of a multi-analytical approach, it was possible to evaluate which and to what extent some chemical and physical paper properties were affected by each single treatment or their combinations. In particular, tensile strength, tearing resistance, DP, colour coordinates, FTIR spectra and SEM features were measured in the blank and treated samples.

The results indicate that γ-rays cause a sizeable DP reduction, but only small colour changes. Indeed, larger colour changes are associated with the synergetic effects of ionising radiation and ageing treatments. Interestingly, in spite of a notable DP decrease, the mechanical properties were found to be affected only slightly, or negligibly, by the γ-irradiation treatment, as well as by thermal drying and ageing treatments. Finally, no clear evidence for changes in the FTIR and SEM features due to the treatments employed was found.

4.1 Introduction

Paper degradation occurs naturally, but degradation processes may be accelerated by a variety of factors, contamination by biodeteriogens being among these. As outlined in Chapters 1 and 3, an appropriate conservation of paper materials should take into consideration the adverse factors which affect their preservation. Environmental conditions, specially temperature and humidity, have dual effects. Certain values of T and RH not only may accelerate physical and chemical degradation, but they may also create a favourable environment for the growth and development of microorganisms, thus causing biodeterioration. Biodeterioration has been defined as any unwanted modification in material properties caused by the vital activities of organisms [1]. The organisms involved are generally called biodeteriogens, and their main characteristic consists in their saprotrophic ability of using a substrate to support their growth and reproduction [2]. Preservation from biodereriogens was already known in Roman times. Vitruvius[23], Plinius the Elder and other Latin and Greek references gave recommendations to protect papyrus from insect attacks, such as the use of cedar oil [5,6].

In general terms, biodeterioration of paper materials is mainly related to the activity of bacteria, fungi and protozoa, insects and rodents to a smaller extent. Numerous genera and species of fungi and bacteria can be found, whose description somewhat falls outside of the aim of the present study, but further details can be found in [5,7].

Recently, biodegradation has been described among the most serious and underappreciated sources of damage to library and archival materials [8]. The environmental conditions often occurring in libraries, archives, and museums promote more the growth of fungi than that of bacteria, fungi requiring less moisture to develop [9]. Biodeteriogens use paper as growth medium finding nutrients necessary to their survival, spending there partially or completely their life cycle. Biodegradation may cause different kinds of damages relying mainly on the organisms responsible for the contamination. In addition, biodeterioration processes depend on the chemical and physical properties of

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[23] Marcus Vitruvius Pollio (circa 80 BC – circa 15 BC), commonly known as Vitruvius, in his De architectura (Book II, Chapter IX, 13) wrote «Item cedrus et iunipirus easdem habent virtutes et utilitates, sed quemadmodum ex cupresso et pinu resina, ex cedro oleum quod cedrium dicitur nascitur, quo reliquae res cum sunt unctae, uti etiam libri, a tineis et carie non laeduntur» [3], whose proposed translation into English is: «The cedar and the juniper tree have the same uses and good qualities, but, while the cypress and pine yield resin, from the cedar is produced an oil called cedar-oil. Books as well as other things smeared with this oil are not hurt by worms or decay», as reported in [4].

paper constituents. As mentioned in Chapter 1, generally, aesthetic, chemical and physical properties may be affected by microorganisms.

Evidence for mechanical damages caused by insect are shown in Figures 3.8 and 3.19. Aesthetic damages, such as those shown in Figure 3.7, can be ascribed to colour changes, due to the activity of bacteria and fungi that synthesise different colourants depending on the species, life cycle stage, presence of other compounds, acidity of the paper substrate, as well as on ventilation and illumination of the latter. Other typical stains, known as foxing, different from those shown in Figure 3.7, are also ascribed to microorganism activity, in which fungi are considered to play a key role [7,10,11]. The term ‘foxing’ generally refers to the paper alteration that manifests in brown, brown-reddish or yellowish spots, whose origins and causes are not clearly understood [12]. The term foxing only vaguely describes the shape and size of stains, its interpretation thus depending on each observer’s judgment [13]. Although originally these spots were called ‘fox spots’ because of their rusty-red colour, similar to fox fur, and their spot-like shape, it seems that over time any disfiguring marks are being included under the term foxing [11]. In a review [14] on the nomenclature of spots, no unifying approach was found. However, generally it has been suggested that old fungal spots are rusty red, while contemporary fungal spots have the colour of their conidia (e.g., black, gray, green) [15]. Two probable explanations, one biotic and the other one abiotic, account for foxing development, the first is attributed to microorganism activity, the latter to oxidation and/or heavy metal deposits [12]. Presence of metals, deriving from papermaking processes or airborne dust, has been considered one of the major causes. Iron, tin and copper were typically identified. However, since 1917 fungal infection has been indicated as a source of foxing. Meynell and Newsam [10] reported for the first time the analysis of foxing through scanning electron microscopy (SEM) in 1978, providing evidence of fungi which were growing on the sizing material. Further microbiological tests indicated that general foxing is caused by xerophilic fungi, whose presence is possible also on non-cellulosic materials, as long as an optimum environment is present [16]. Moreover, the results obtained using jointly FTIR, microscope, and mycological analyses of stained cardboards strongly support the biotic origin of foxing [17].

Chemical and structural changes due to fungal activity are mainly ascribed to the production of compounds, namely, cellulase enzymes which catalyse enzymatic hydrolysis [18,19]. The production of these extracellular enzymes, consisting of esoglucanase, endoglucanase and β-glucosidase, and their synergetic interaction involve the enzymatic deterioration of crystalline cellulose, whereas other cellulolytic fungi, that do not synthesise such enzymes, act only on amorphous cellulose [18]. Water absorption promotes swelling of the fibres, allowing bacteria and fungi to set themselves in the amorphous region. Many biodeteriogens are able to hydrolyse hemicelluloses, while a few species of bacteria and fungi decompose lignin. Therefore, the reactivity of cellulosic fibres to biodeteriogens is determined by numerous factors accounting for intermolecular and interfibre bonding, such as degree of polymerisation, degree of crystallinity, chain orientation, cross-linking and functional groups [20]. In this regard, it is worth introducing the term ‘bioreceptivity’ which generally refers to the aptitude of a material to be colonised by living organisms, regardless of biodeteriodation processes that they could cause [21]. Therefore, on the basis of the above considerations, cellulose containing a large number of amorphous sites along the polymer has an higher bioreceptivity than that with more crystalline sites, as amorphous regions are more susceptible to biodeterioration. Also the removal of lignin from pulps, albeit generally contributes to an increase of paper quality, amplifies the bioreceptivity, since lignin increases the resistance of cellulose to the attack of microorganisms [9,18]. Moreover, significant differences were observed between paper with different sizing and fillers, suggesting that also these non-cellulosic components influence the fungal growth affecting paper hygroscopicity [2,18]. Generally, in fact, biodegradation occurs when the MC of paper approaches 10%, the higher is the paper hygroscopicity the lower will be the RH (%) to which 10% of free water can be reached [18]. Acidic pHs are generally reported to stimulate the fungal growth, although the optimum pH strongly varies among the species [18], that of specific groups of ascomycetes being between 7.1 and 10.4 [2]. Therefore, the material composition, conservation state together with environmental parameters, such T and RH, are among the factors to be considered for the colonization and establishment of any biological community [8]. In a recent review [9], it has been reported that, according to the literature, the growth of fungi can be prevented by providing good air circulation, and keeping T under 20 °C and RH under 60% (which corresponds to a water activity[24] of a paper object equal to 0.60, if this object is in equilibrium with the surrounding atmosphere). This maximum value of RH, also suggested by the standard ISO 11799 [23], is specifically aimed at reducing the risk of microbiological activity.

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[24] In this context, the expression “water activity” refers to the water available to the microorganisms and the atmosphere in which they grow. It is defined as the ratio between the vapour pressure of water over the material and the vapour pressure over pure water at the same temperature [22].

Furthermore, it should not be underestimated that the presence of fungi may represent risks also to human health [24], many of these microorganisms being pathogenic and toxinogenic [25].

Stopping the proliferation of these microorganisms is not an easy task both because of its relationship with improper storage conditions, and drawbacks of the disinfection techniques so far devised. As far as the former issue is concerned, it is worth mentioning a study [26] conducted at the library of the Jasna Góra monastery in Częstochowa, the most important sanctuary in Poland. The results revealed that the environment, without any air-conditioning system or control of the microclimatic parameters, was once again microbiologically contaminated 10 years after disinfection of the incunabula collection by ethylene oxide in a pressure chamber. In particular, the indoor fungal pollution was related to the unrestrained infiltration of ambient air through the draughtiness of building envelops, while bacterial contamination was attribute to sources in the indoor environment [26].

Generally, an ideal antifungal method ought to have a broad activity spectrum, good chemical stability, prolonged effects, low cost, but at the same time, it should not provoke adverse side effects on humans and treated materials [9]. In addition, it is to be noted that antifungal treatments can be applied to both single objects and mass disinfection, being thus potentially applicable as a preventive measure before incorporation in an institution, a periodic curative procedure, or as a recovery measure after emergency situations. As far as the latter circumstances are concerned, unfortunately more than a few extreme and catastrophic events occurred in the last five decades that required disinfection treatments of a considerable number of books. It is worth remembering the devasting flood of the Arno river that in November 1966 compromised numerous libraries and archives, the flood of the Tanaro river in November 1994, which immersed the library-archive of Cesare Pavese [27], the more recent flood, dated summer 2002 in Prague, which damaged about fifty libraries, including the National Library of the Czech Republic [28]. Again, other events due to aqueous fire suppressions, like after the fire of the Los Angeles Central Library [27]. These events require a viable technology for the recovery and disinfection of large amounts of biodegraded (or potentially biodegraded) materials, such as 2000 m^3 of paper documents after the Czech flood and 700 thousand books after the fire at the Central Library of Los Angeles [27].

Most of the methods implemented to avoid fungal deterioration of archival and library materials have been adapted from other scientific fields such as agriculture or medicine. A recent review [9] provides a description of the most common methods, grouping them into chemical and physical methods. For further details on possible methods, the reader can refer to the review by Sequeira et al. [9]. A summary of some methods is presented below with particular attention to the controversy over the use of γ-rays, object of the present study.

Chemical methods mainly consist in the application of gaseous or liquid chemicals that interact with specific target sites on and in the microbial cell. Most of these microbicides can be classified as membrane- or electrophilically active, according to their mechanism of action [29]. The former type includes alcohols, phenols and other compounds that act by coating the cell wall adsorptively. These adsorption processes cause changes in the outer membrane and along the cell wall that eventually looses its integrity, allowing the microbicides to access to the cytoplasmic membrane, where they release their lethal effects [29]. On the other hand, electrophilically active microbicides include aldehydes, organometals and other compounds, that are attracted to components in the microbial cell with high electron density, such as nucleophilic components. These microbicides lead to the inactivation of enzymes through electrophilic addition or substitution [29].

Alcohols, such as butanol, isopropanol and ethanol, have been widely used for disinfection of paper materials at different concentrations and with different procedures (e.g., spraying, brushing, swabbing or exposure to vapours) [9,30,31]. However, given that alcohols do not seem to be effective against sporulating microorganisms, they can be considered as disinfecting agents, not as sporicidal [31]. In addition, it has been reported that effects of alcohols vapours on thick materials, such as books, cannot be effective [31]. As far as the adverse effects of alcohols on paper materials are concerned, changes may derive especially from application by immersion, due to extraction of soluble components, while feathering of ink was observed even with vapour application [31]. In this regard, it has been suggested that, although no deleterious effect on filter paper treated with a concentration of 70% ethanol was observed, each material should be thoroughly tested before the treatment, as undesirable reactions, such as dissolution, may take place [32]. Very recently, it has been reported that the disinfection of paper pieces with a process that employs supercritical carbon dioxide and addition of 4% ethanol (w/w) could be a very promising option for preservation and control of fungi of ancient documents [33]. However, the use of supercritical carbon dioxide is not diffuse at a commercial scale because of the high capital investment required for this technology [33].

Ethylene oxide has also been widely used due to its microbiologic inactivation properties related to alkylation reactions of cellular constituents, such as nucleic acids and functional proteins, causing their denaturation [34]. It has been described as an exceptional sterilizing agent because of its effective bactericidal, sporicidal and virucidal activity, although its use can not ignore the potential hazards to humans and environment, as well as risks related to handling a flammable gas [34]. Fumigations of mixtures of ethylene oxide and other gases (such as carbon dioxide) could be carried out at several pressures (e.g., normal pressure, vacuum or pressurised chamber), temperatures (e.g., from 20 to 37 °C) and exposure times (e.g., from 3 to 24 h) [9]. However, air washing cycles are necessary after the fumigation to remove as much of the residual ethylene oxide as possible because of its toxicity and that of its derivatives. Indeed, the International Agency for Research on Cancer (IARC) has classified ethylene oxide as carcinogenic to human (group 1) [35]. Moreover, as summarised in the above-mentioned review [9], physical and chemical changes of paper treated by fumigation with ethylene oxide were shown (folding endurance, degree of polymerisation, colour and acidity being affected), and archive materials treated with ethylene oxide was considered to be more susceptible to microbial attack.

Physical methods for disinfection require no application of chemical compounds, for this reason no residue is left on paper, but at the same time, their action is exerted for a limited time. Generally, in addition to the physical methods such as freeze-drying [28], use of radiation has become widely used in disinfection treatments [9]. The use of radiation for sterilisation was already known by the end of the 19th century and beginning of the 20th century [36]. UV-irradiation, using an excimer laser operating at 308 nm as UV-ray source, has been proposed as a novel sterilization technique for cultural heritage [37].

γ-irradiation is often used as a sterilizer in other fields such as medicine, pharmacy and agriculture. ^{60}Co, a radioisotope that continuously emits γ-rays, is generally used. This radiation, capable of a high penetration power, is able to cleave C–C bonds, destroying cellular DNA, and thus leaving cells non-viable [38]. Therefore, ionising radiation through denaturation devitalises simultaneously and indiscriminately all living organisms present in and outside the material treated [39]. As reported in [9,39,40] one of the first application of γ-irradiation for paper disinfection of archive documents infested by fungi is dated back to 1960 [41]. The use of gamma ionising radiation experienced a long-time pause because of the diffusion of sterilisation treatments through fumigant gases (such as ethylene oxide), but was promptly restored when the harmful effects on humans caused by these gases were discovered [39].

Numerous studies performed over the last 30 years were carried out to investigate γ-irradiation in terms of its efficiency as a disinfection treatment, the minimum lethal dosage, and effects on chemical and physical properties of different kinds of paper [19,40,42–52]. The general consensus is that γ-radiation affects paper properties (such as degree of polymerisation and colour) by the same mechanisms that work on microorganisms. The application of γ-irradiation for books and documents preservation is still a source of controversy. The effects of γ-irradiation at different doses (0, 1, 2, 5 and 10 kGy) were compared with those of fumigation with ethylene oxide, concluding that ionising radiations cause negative effects both on DP and colour, depending on the dose absorbed, while acidity and tensile strength are not affected even by high doses [43]. Although no effects on the properties measured in that study were found after fumigation with ethylene oxide, the authors encourage the assessment of feasibility for future treatment with low doses of ionizing rays in the recovery of biodeteriorated books, since the ban on the use of ethylene oxide already occurred in some countries [43]. Adamo and co-authors [44] later reported that the negative effects caused by γ-irradiation did not significantly affect the basic properties of a good printing paper, suggesting a dose of 2-3 kGy. In another study [46], in which different kinds of paper were irradiated at a 14.4 kGy dose, it was found that the deterioration of mechanical properties and colour changes in magazine paper were not significant. The authors thus concluded that accelerated ageing introduced larger damages in mechanical properties than the irradiation treatment [46]. Recently, the effects of γ-irradiation at different doses (2, 6, 10 and 11 kGy) on chemical and physical properties of three different kinds of paper were investigated [51]. The results indicated that the γ-irradiation treatment with doses in the range 4-6 kGy, at any dose rate, produced no critical changes in the physical properties of the papers. Therefore, it was concluded that a regular use of documents and books would not be affected [51]. The efficiency of additional treatments before γ-irradiation was also investigated [40]. It was reported that a pre-treatment, in which the paper was exposed to high humidity and temperature (i.e., 50 °C and 95% of RH for 24 h), favoured germination of dormant fungal spores, instead of no pre-treatment (room conditions) or drying pre-treatment (at 50° C per 24 h) [40]. Moreover, irradiation doses at low levels (< 10 kGy) were not found to influence appreciably the growth of fungi after the irradiation treatment, the fungal growth being comparable to the non-irradiated control. On the contrary, higher doses (100 and 200 kGy) can induce structure alterations that may affect fungal growth [47]. The effects of higher doses of γ-rays, ranging from 10 to 50 kGy, were tested on the mechanical properties of Korean traditional paper [48], no significant change in tensile strength, bursting strength and appearance being detected. Experiments at the dosage used by the US Postal Service to treat mail, and even higher doses (up to 250 kGy), were carried out on three woodfree paper samples. A linear relationship between the number of chain scissions in cellulose and the dose was found [53]. However, as clearly pointed out by Area and co-authors [51], such tests have been performed with extremely high doses, well above those used for removal of microorganisms. Indeed, as far as the effective dose for fungi disinfection is concerned, it is generally agreed that a satisfactory disinfection occurs at irradiation dose of 5 kGy [51,52], while Moise and co-authors [49] concluded that a dose range of 5-7 kGy, at the same time, guarantees a significant decrease of biodeteriogens and minimise negative effects. In contrast, other authors draw the opposite conclusion, i.e., γ-radiations, even at the minimum dosage required for disinfection, would cause degradative effects so pronounced to make this technique inadvisable [52,54]. Although the stimulating question about the use of γ-irradiation was reopened by Sinco in 2000 [55] and numerous following studies, an unanimous agreement on the use of this method as a disinfection treatment has not yet been found, the question remaining open.

4.2 Aim of the study

The most appropriate and effective treatment of mass disinfection of paper materials against microorganisms is still a controversial issue in the scientific literature. In particular, studies of the use of γ-radiation as a suitable method for such purposes draw opposite conclusions, suggesting or not its use on archival and library materials. In this context, the present study, already published [56], was carried out to investigate the effects of γ-irradiation together with additional treatments on model paper, thus evaluating the applicability of γ-irradiation as disinfection treatment.

4.3 Material and Methods

4.3.1 Paper types and treatments

Chromatography paper MN 261 (Macherey-Nagel, Germany), made of pure cellulose, ash and lignin free, was used. Paper samples underwent three different treatments, i.e., γ-irradiation, thermal drying and ageing, according to the scheme described below (see Table 4.1). Before any treatment, paper samples were conditioned at 14% water content.

As mentioned above, it is generally agreed that a satisfactory disinfection occurs at irradiation doses of about 5 kGy, more resistant fungi requiring higher doses [51,52]. Therefore, the irradiation of paper samples was carried out using a ^{60}Co source at two different doses, i.e., 5 and 10 kGy, in an industrial apparatus[25], as described elsewhere [57]. The thermal drying treatment was performed, after irradiation, in a climatic chamber (Book's Wind 2 – Frati & Livi) and consisted in heating paper samples at 60 °C for 20 h. The residual water content of the dried paper was 8%. Finally, two ageing treatments were carried out, after irradiation, at the thermo-hygrometric conditions suggested by the standard ISO 5630-3 [58], 80 °C and 65% RH, one for 24 h and the other one for 144 h.

4.3.2 Experimental design of the treatments

Samples were treated in such a way that all the combinations of the treatments could be evaluated, as reported in Table 4.1.

Table 4.1. Treatments to which samples were subjected [56].

Sample	γ-dose (kGy)	Thermal drying	Ageing
1	0		
2	5		
3	10		
4	0	yes	
5	5	yes	
6	10	yes	
7	0		24h
8	5		24h
9	10		24h
10	0	yes	24h
11	5	yes	24h
12	10	yes	24h
13	0		144h
14	5		144h
15	10		144h
16	0	yes	144h
17	5	yes	144h
18	10	yes	144h

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[25] The exposure of contaminated paper samples to γ-rays was performed at Sterigenics Italy S.p.A.

Therefore, for each irradiation dose (i.e., 0, 5 and 10 kGy), one sample set received no ageing, one was aged for 24 h and another one for 144 h. In addition, for each dose and ageing set, one additional sample set received the thermal drying treatment. The effects of each single physical treatment were thus evaluated, as well as possible synergetic effects.

4.3.3 Methods for evaluation of degradation effects

Destructive and non-destructive techniques[26] were employed to evaluate the effects on chemical and physical properties of paper samples treated using γ-irradiation, thermal drying, ageing, and their combinations. In particular, both for the untreated sample (blank) and all treated samples, tensile strength, tearing resistance and DP were measured destructively, while colour, FTIR spectra and SEM features were obtained non-destructively [56].

4.3.3.1 Mechanical tests

Mechanical properties have been evaluated in numerous studies dealing with both the application of gamma radiation as disinfection treatment, and ageing experiments. In this study, tensile strength (TS) and tearing resistance (TR) were measured following, respectively, the standard procedures ISO 1924-2 [59] and ISO 1974 [60]. For each mechanical property, 10 measurements were carried out on paper strips (width=15 mm, length=180 mm). The determination of tensile strength was carried out using an Instron dynamometer, while tearing resistance was determined by an Elmendorf pendulum.

4.3.3.2 Viscometry

As reported by Adamo and co-authors [43], undoubtedly, viscometry is a very sensitive and practical method because it allows to evaluate the depolymerisation immediately after the treatment with γ-radiation. In addition, as reported in the previous Chapters, this method is generally used to estimate the degradation extent of paper-based materials. In the present study, all paper samples, untreated and treated, were analysed viscometrically according to the standard procedure ISO 5351 [61]. An appropriate mass of paper sample was dissolved in a known volume of 0.5 M CED/water solution, as

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[26] Mechanical tests were carried out by Prof. Maurizio Fiorini and collaborators at the Department of Civil, Chemical, Environmental and Materials. FTIR, SEM and colour measurements were performed at the Conservation Science Laboratory for Cultural Heritage of the University of Bologna.

discussed in Chapter 2. The solution was then inserted into a capillary-tube viscometer (Ubbelohde, 532 10 I), thermostated at 25.0 ± 0.1 °C, as shown in Figure 2.3. By measuring the efflux time, η_r was obtained, leading to the determination of $[\eta]$, knowing the mass concentration. Thus, DP values were calculated by means of Mark-Houwink-Sakurada equation (see Eq. 1.1) [62], with the set of parameters proposed by Evans and Wallis [63] (see Eq. 2.1). Each DP value was obtained from two samples, and two measurements for efflux time were carried out for each sample. The uncertainty of DP determination was evaluated to be ±2%.

4.3.3.3 Colorimetry

A portable spectrometer (Minolta, CM-2600d) was used for colour measurements. This instrument, equipped with an internal integrating sphere of 56-mm diameter in reflectance geometry d/8, and three Xenon pulsed lamps, was operated in the specular component mode, as for colour measurements described in Chapter 2. Reflectance spectra were measured in the 400-700 nm range, with a resolution of 10 nm, and using the D65/10° measurement condition [64]. A white plate (Minolta, CM-A145) was used for the calibration. In this study, three spectra were measured on three different points of each sample. The data of each untreated and treated samples were processed using SpectraMagicTM NX (Version 2.7) and Microsoft Excel software to evaluate the CIELAB colour coordinates [65]. Although the CIELAB system has been described in Chapter 2, it is worth recalling briefly that, according to this system, the colour space (see Figure 2.4), is defined by the three coordinates L^*, a^* and b^* which, respectively, represent the lightness, redness-greenness and yellowness-blueness axes [65]. The changes of these coordinates in the treated samples indicate the effects of each treatment and their combinations on the colour. In this study, as in Chapter 2, the colour differences, ΔE^*_{ab} and ΔE_{00}, were calculated using two different formulas. The former expresses the geometric distance of two points in the CIELAB space and is calculated with Eq. 2.2 [66], while ΔE_{00} is the colour-difference formula proposed more recently [67], calculated using Eq. 2.3. ΔE_{00} values were calculated through the Microsoft Excel implementation available online [68], described by Sharma and co-authors [69].

4.3.3.4 SEM

Images were acquired with secondary and back-scattered electron detectors using a Quanta Inspect S FEI instrument, operating at a voltage of 15 kV with a tungsten filament current of 100 µA. Areas of each treated and untreated sample were analysed at different magnifications in order to identify possible changes in the surface morphology of the cellulose fibres.

4.3.3.5 FTIR spectroscopy

Infrared spectroscopy is not only useful to characterise paper, but also to detect changes due to degradation processes, as mentioned in the previous Chapters and reported in several studies [70–73].

In the present study, a Tensor 27 spectrometer was used with OPUS software (Version 7.2) to acquire FTIR spectra in attenuated total reflectance (ATR). Each spectrum was acquired as an average of 64 scans over the 400-4000 cm^{-1} range, with a resolution of 4 cm^{-1}.

4.3.4 Statistical analysis

A multi-factor analysis of variance (ANOVA) was employed to test statistically the differences [74] between the data supplied by ΔE^*_{ab} and mechanical tests for the untreated and treated samples, accounting for γ-irradiation, drying and ageing treatments. This statistical analysis was performed using Statgraphics plus (Version 2.1) and the differences between the means were evaluated using the least significant difference (LSD) test with a significance level of $\alpha=0.01$.

4.4 Results and Discussion

4.4.1 Mechanical properties

The effects of γ-irradiation, thermal drying and ageing treatments on the mechanical properties were evaluated considering also possible synergetic effects. Figure 4.1 shows the tensile strength and tearing resistance values measured for all samples, according the scheme reported in Table 4.1.

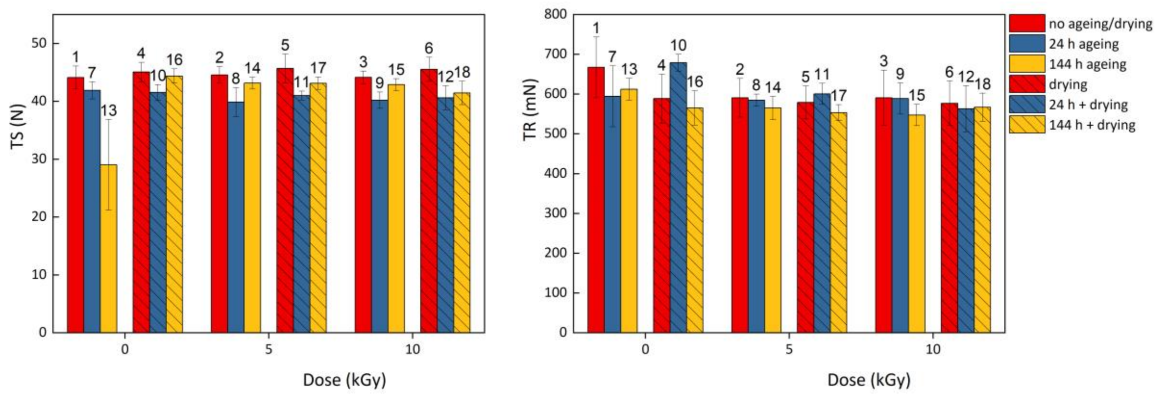

Figure 4.1. Tensile strength (TS, left) and tearing resistance (TR, right) as a function of γ-dose with the vertical lines indicating the standard deviations. For each dose (0, 5 and 10 kGy), the colours of the bars indicate the additional ageing treatment: red, blue and yellow for unaged, 24-h aged and 144-h aged, respectively. The bars with oblique lines, corresponding to the right-side triplet, received also the thermal drying treatment. The numbers above the bars identify the paper sample according to the scheme reported in Table 4.1. Adapted from [56].

It is to be noted that the value for sample 13 (i.e., aged for 144 h) is particularly small, although it is characterised by a large variance. Except for this sample, the differences between the measured tensile strengths are relatively small, most of them falling within the evaluated standard deviation intervals. Therefore, γ-irradiation at 5 and 10 kGy does not essentially affect the tensile strength, in line with the results reported by Adamo and co-authors [43]. In general, ageing causes a small (less than 10%) reduction of the tensile strength, while thermal drying and γ-irradiation increase it, but the differences are very small and vary within the reference groups.

As far as the tearing resistance is concerned, it can be noted that γ-irradiation caused a small (less than 10%) decrease in the tearing resistance values, no evident effect being observed from 5 to 10 kGy dose. Moreover, the longest ageing treatment (i.e., 144-h ageing) slightly reduces the tearing resistance. No evidence for synergetic effects between irradiation and thermal drying treatment was detected. In general terms, also for tearing resistance, most of the measured values are equal to each other accounting for the evaluated internal variances.

4.4.2 DP

The DP values determined for all samples are reported in Table 4.2, where, for the sake of clarity, the treatments received by each sample are also reported. These values are also displayed in the graph of Figure 4.2.

Table 4.2. DP values with the standard deviations, and the treatments to which each sample was subjected [56].

Sample	γ-dose (kGy)	Thermal drying	Ageing	DP
1	0			1730 ± 35
2	5			1093 ± 19
3	10			962 ± 19
4	0	yes		1734 ± 35
5	5	yes		1035 ± 21
6	10	yes		900 ± 18
7	0		24h	1706 ± 34
8	5		24h	1046 ± 21
9	10		24h	918 ± 18
10	0	yes	24h	1726 ± 35
11	5	yes	24h	991 ± 20
12	10	yes	24h	872 ± 17
13	0		144h	1695 ± 34
14	5		144h	976 ± 20
15	10		144h	865 ± 17
16	0	yes	144h	1691 ± 34
17	5	yes	144h	929 ± 19
18	10	yes	144h	797 ± 16

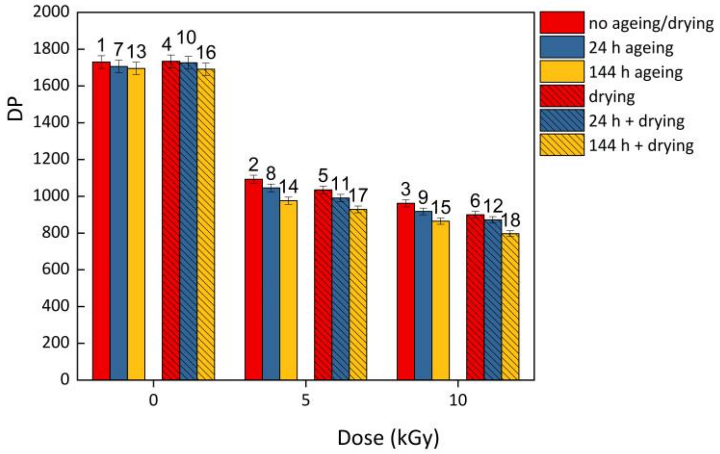

Figure 4.2. DP as a function of γ-dose with the vertical lines indicating the standard deviations. For each dose (0, 5 and 10 kGy), the colours of the bars indicate the additional ageing treatment: red, blue and yellow for unaged, 24-h aged and 144-h aged, respectively. The bars with oblique lines, corresponding to the right-side triplet, received also the thermal drying treatment. The numbers above the bars identify the paper sample according to the scheme reported in Tables 4.1 and 4.2. Adapted from [56].

Unlike mechanical properties, at first sight, it is evident that a 5-kGy dose causes a considerable decrease of DP, the further effect produced by the higher dose of 10 kGy being relatively small. Such a notable DP decrease could seem in contrast with the relatively small changes observed in the mechanical properties. However, the present data are in line with the results reported by Strlič and co-authors [75], for which mechanical deterioration appears to accumulate at very low rate, randomly and independently of DP, for paper with DP > 800. Indeed, it can be noted that although the 5-kGy dose reduced DP by somewhat more than 40%, the absolute value of DP (about 1000) is still large relative to the threshold value of 300, at which paper objects are no longer suitable for use, as suggested by Strlič and co-authors [75]. Small but non-negligible effects are related to both ageing and thermal drying treatments on the irradiated samples, the sample 18 with the lowest DP value (about 800) being the one irradiated at 10 kGy, 144-h aged and thermally dried. No effects on the non-irradiated samples in terms of DP due to the additional treatments of ageing and thermal drying were detected.

4.4.3 Colour changes

Paper degradation can be accompanied by colour changes, as discussed in the previous Chapters. Yellowing is generally ascribed to the formation of carbonyl groups (aldehydic and ketonic) [76,77] and reduction of the HOMO/LUMO energy gap, with consequent absorption in the visible region. In this study, colour changes were evaluated in terms of the CIELAB colour coordinates, and colour differences (i.e., ΔE^*_{ab} and ΔE_{00}).

Table 4.3. Colour coordinate L^*, a^* and b^* with their standard deviations, and the treatments to which each sample was subjected [56].

Sample	**γ-dose (kGy)**	**Thermal drying**	**Ageing**	**L^***	**a^***	**b^***
1	0			97.67 ± 0.06	0.16 ± 0.01	2.31 ± 0.02
2	5			97.30 ± 0.02	0.24 ± 0.01	2.80 ± 0.03
3	10			97.15 ± 0.03	0.26 ± 0.01	3.02 ± 0.02
4	0	yes		97.65 ± 0.04	0.16 ± 0.01	2.32 ± 0.03
5	5	yes		97.23 ± 0.02	0.23 ± 0.01	3.00 ± 0.05
6	10	yes		97.05 ± 0.05	0.23 ± 0.01	3.23 ± 0.02
7	0		24h	96.92 ± 0.07	0.24 ± 0.01	3.22 ± 0.06
8	5		24h	95.80 ± 0.03	0.47 ± 0.01	4.04 ± 0.03
9	10		24h	95.33 ± 0.01	0.52 ± 0.01	4.45 ± 0.01
10	0	yes	24h	97.25 ± 0.01	0.21 ± 0.01	2.65 ± 0.05
11	5	yes	24h	95.60 ± 0.01	0.50 ± 0.01	4.22 ± 0.04
12	10	yes	24h	95.17 ± 0.02	0.56 ± 0.01	4.64 ± 0.03
13	0		144h	96.78 ± 0.01	0.38 ± 0.01	3.04 ± 0.02
14	5		144h	93.89 ± 0.05	0.79 ± 0.01	5.10 ± 0.03
15	10		144h	93.22 ± 0.13	0.86 ± 0.04	5.73 ± 0.17
16	0	yes	144h	96.81 ± 0.02	0.36 ± 0.01	3.02 ± 0.04
17	5	yes	144h	93.51 ± 0.05	0.85 ± 0.01	5.44 ± 0.03
18	10	yes	144h	92.62 ± 0.06	1.03 ± 0.01	6.18 ± 0.09

The colour coordinates L*, a* and b* of the untreated and treated samples are reported in Table 4.3, where the treatments received by each sample are also reported. Figures 4.3 and 4.4 show the trends of L*, a* and b*, accounting for all the treatments carried out.

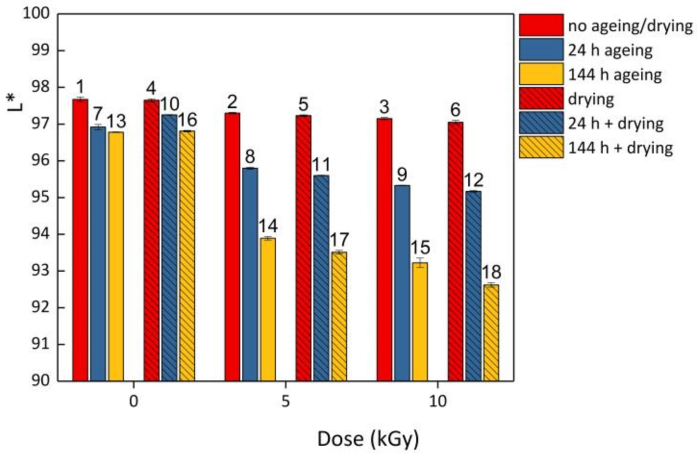

Figure 4.3. L component as a function of γ-dose with the vertical lines indicating the standard deviations. For each dose (0, 5 and 10 kGy), the colours of the bars indicate the additional ageing treatment: red, blue and yellow for unaged, 24-h aged and 144-h aged, respectively. The bars with oblique lines, corresponding to the right-side triplet, received also the thermal drying treatment. The numbers above the bars identify the paper sample according to the scheme reported in Tables 4.1 and 4.3.*

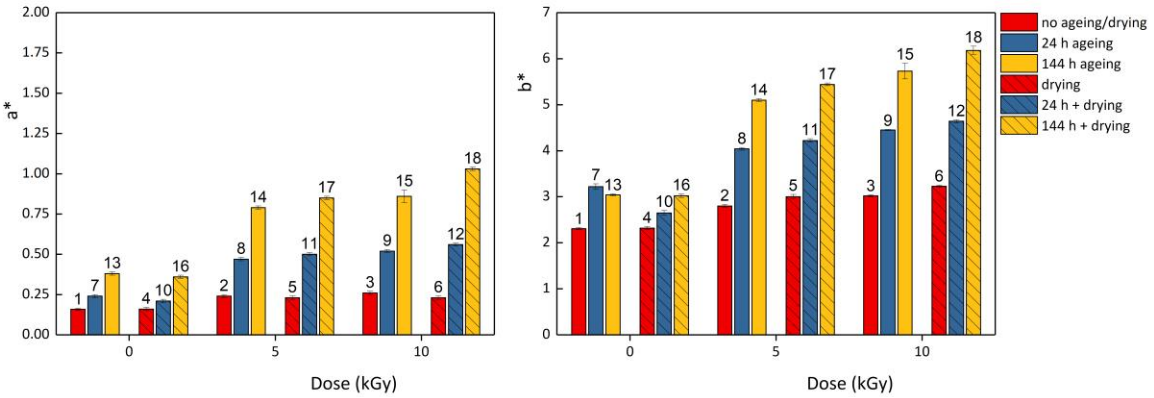

Figure 4.4. a(left) and b* (right) component as a function of γ-dose with the vertical lines indicating the standard deviations. For each dose (0, 5 and 10 kGy), the colours of the bars indicate the additional ageing treatment: red, blue and yellow for unaged, 24-h aged and 144-h aged, respectively. The bars with oblique lines, corresponding to the right-side triplet, received also the thermal drying treatment. The numbers above the bars identify the paper sample according to the scheme reported in Tables 4.1 and 4.3.*

It is evident that the L* component, indicating the lightness, decreases, as expected, but interestingly the main changes are related to the ageing treatments on the irradiated samples. On the contrary, the a* component increases, as well as the b* component, but again the main changes can be associated with the effects of ageing treatments on the irradiated samples. Generally, a negative trend of the L* component indicates that the analysed sample reflects less light than the reference surface (e.g., sample 1), while positive trends of the a* and b* components point out that the analysed sample is more red and yellow, respectively, than the reference surface. The present results are in line with previously reported studies [52,78]. However, it is worth noting that the trend of the a* component obtained on the model paper used in this study differs from that obtained using contemporary paper (see Figure 2.1), discussed in Chapter 2. In this regard, it should be noted that also Castro and co-authors measured different trends of the a* component, depending upon the kinds of paper (specifically, positive for Whatman and negative for newsprint paper) [78], which could thus be ascribed to additives used in the manufacturing of contemporary papers.

As far as the colour differences is concerned, Table 4.4 reports ΔE^*_{ab} and ΔE_{00} values calculated according to Eq.s 2.2 and 2.3, respectively. It is to be noted that two values for each colour difference are reported, i.e., ΔE^*_{ab} and ΔE_{00} determined relative to the untreated sample (sample 1: no gamma, no drying, no ageing), and $\Delta E^*_{ab(ref)}$ and $\Delta E_{00(ref)}$ relative to the non-irradiated sample within each reference group receiving the same additional treatments (thermal drying and ageing). The results are also visually displayed in Figures 4.5 and 4.6.

Table 4.4. Colour differences express as ΔE^*_{ab} and ΔE_{00} relative to sample 1 (no γ-rays, no drying and no ageing), and as $\Delta E^*_{ab\,(ref)}$ and $\Delta E_{00\,(ref)}$ relative to the non-irradiated sample within each reference group receiving the same additional treatments (thermal drying and ageing) [56].

Sample	**γ-dose (kGy)**	**Thermal drying**	**Ageing**	ΔE^*_{ab}	ΔE_{00}	$\Delta E^*_{ab\,(ref)}$	$\Delta E_{00\,(ref)}$
1	0			-	-	-	-
2	5			0.62	0.50	0.62	0.50
3	10			0.89	0.72	0.89	0.72
4	0	yes		0.02	0.01	-	-
5	5	yes		0.82	0.67	0.80	0.66
6	10	yes		1.11	0.90	1.09	0.89
7	0		24h	1.18	0.93	-	-
8	5		24h	2.57	1.92	1.41	1.02
9	10		24h	3.19	2.36	2.03	1.46
10	0	yes	24h	0.54	0.40	-	-
11	5	yes	24h	2.84	2.11	2.30	1.72
12	10	yes	24h	3.44	2.55	2.90	2.15
13	0		144h	1.17	0.89	-	-
14	5		144h	4.74	3.38	3.57	2.50
15	10		144h	5.66	4.02	4.49	3.15
16	0	yes	144h	1.13	0.86	-	-
17	5	yes	144h	5.25	3.74	4.12	2.89
18	10	yes	144h	6.42	4.56	5.29	3.72

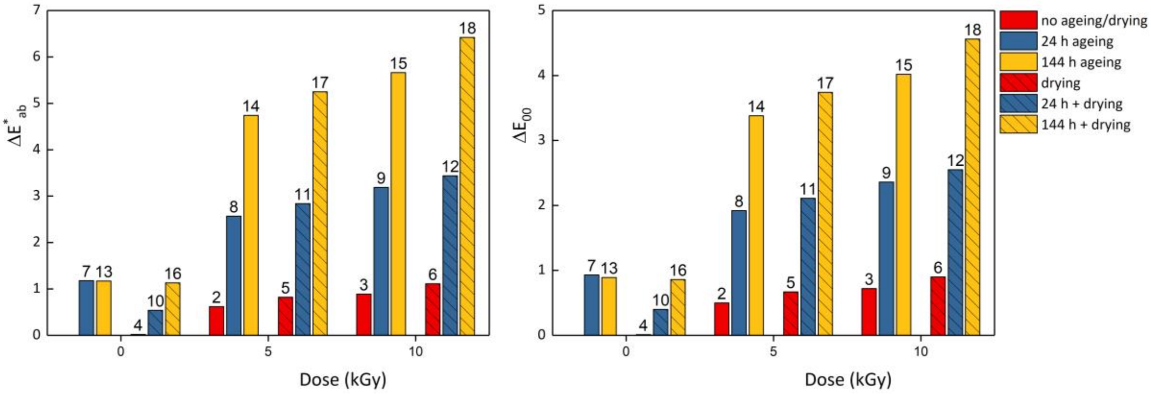

Figure 4.5. ΔE^*_{ab} *(left) and* ΔE_{00} *(right) as a function of γ-dose with the vertical lines indicating the standard deviations. For each dose (0, 5 and 10 kGy), the colours of the bars indicate the additional ageing treatment: red, blue and yellow for unaged, 24-h aged and 144-h aged, respectively. The bars with oblique lines, corresponding to the right-side triplet, received also the thermal drying treatment. The numbers above the bars identify the paper sample according to the scheme reported in Tables 4.1 and 4.4.*

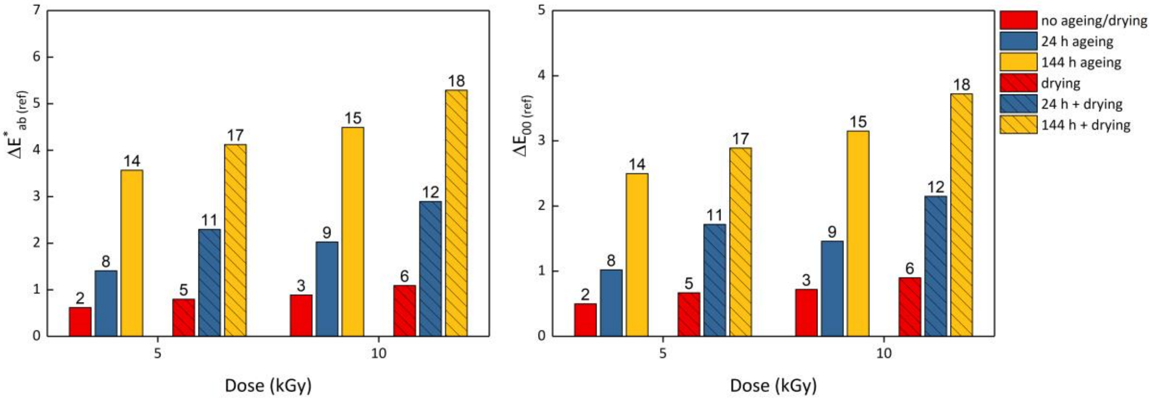

Figure 4.6. $\Delta E^*_{ab(ref)}$ *(left) and* $\Delta E_{00(ref)}$ *(right) as a function of γ-dose with the vertical lines indicating the standard deviations. For each dose (0, 5 and 10 kGy), the colours of the bars indicate the additional ageing treatment: red, blue and yellow for unaged, 24-h aged and 144-h aged, respectively. The bars with oblique lines, corresponding to the right-side triplet, received also the thermal drying treatment. The numbers above the bars identify the paper sample according to the scheme reported in Tables 4.1 and 4.4.*

As mentioned in Chapter 2, the interpretation of ΔE, both in terms of ΔE^*_{ab} and ΔE_{00} , is not straightforward. The literature reports different values of JND, several authors including it between 2 and 4 for ΔE^*_{ab} [52,79], while according to Hardeberg [80] perceptual impact of ΔE^*_{ab} is as follows: < 3 hardly perceptible; 3-6 perceptible but acceptable; > 6 not acceptable. On the basis of these considerations, ΔE^*_{ab} values > 3 (perceptible colour difference) were found in the 144-h aged samples irradiated at 5 and 10 kGy, and in the 24-h aged samples irradiated at 10 kGy, with and without thermal drying. ΔE^*_{ab} reached its maximum value of 6.43 (not acceptable difference) in sample 18 (irradiated at 10 kGy, thermally dried, 144-h aged). Considering the differences within each reference group, $\Delta E^*_{ab(ref)}$ values > 3 resulted only for the irradiated samples aged for 144 h.

As far as the more recent colour difference formula is concerned, ΔE_{00}=1.5 has been suggested as the threshold value for visible perception of colour variations through experiments carried out at the Victoria & Albert Museum [81]. In the present study, ΔE_{00} values > 1.5 were found in the same samples with ΔE^*_{ab} values > 3, and in samples 8 and 11 (irradiated at 5 kGy, 24-h aged, without and with thermal drying, respectively). When the differences within each reference group are considered, $\Delta E_{00(ref)}$ values > 1.5 resulted not only for the irradiated samples aged for 144 h but also for those aged for 24 h and thermally dried. The above results suggest, as a general comment, that the threshold for perceptibility of 1.5 for ΔE_{00} would seem more sensitive than the threshold of 3 for ΔE^*_{ab}.

Furthermore, Figure 4.7 shows the synergic effect between irradiation and ageing, as already indicated by the trends of the single colour components (see Figures 4.3 and 4.4).

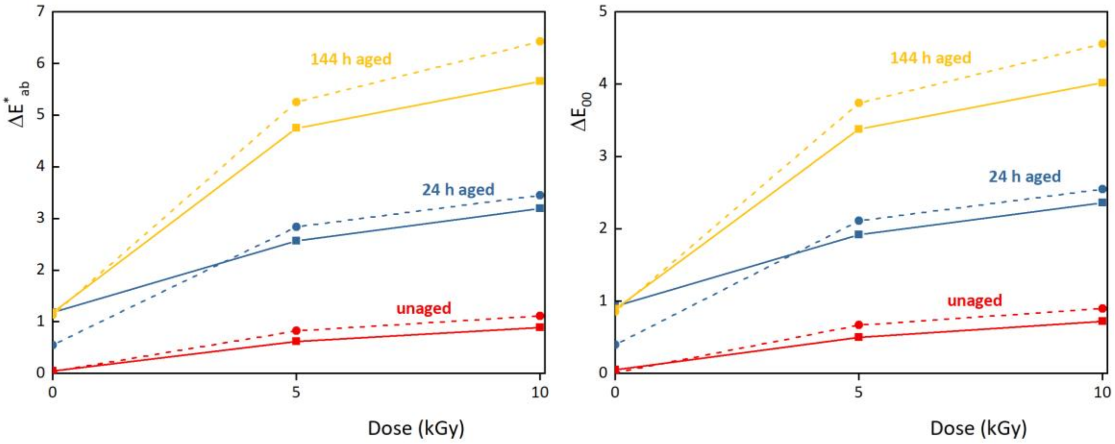

Figure 4.7. ΔE^*_{ab} (left) and ΔE_{00} (right) as a function of γ-ray for samples exposed to thermal drying (dashed lines) and no thermal drying (continuous lines). The colours of the lines indicate the additional ageing treatment: red, blue and yellow for unaged, 24-h aged and 144-h aged, respectively. Adapted from [56].

4.4.4 SEM and FTIR spectroscopy

SEM images, shown in Figure 4.8, do not provide evidence for differences in the shape or arrangement of the fibres after the various treatments suffered by the samples, in line with the data reported by Gonzalez and co-authors [46].

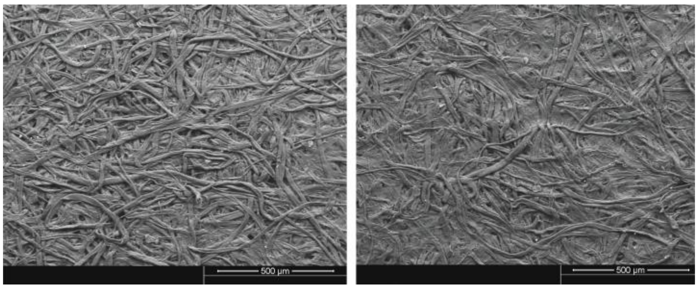

Figure 4.8. Back-scattered electron SEM images of sample 1 (left, blank) and sample 18 (right, irradiated at 10 kGy, thermally treated, 144-h aged). Adapted from [56].

FTIR spectra of untreated and treated samples were compared, and no apparent variations in the relative intensities of the spectral features in the 400-4000 cm^{-1} range were detected. The spectra of samples 1 (untreated) and 18 (irradiated at 10 kGy, thermally treated, 144-h aged), normalized on the most intense feature (1027-1255 cm^{-1}), are shown in the left side panel of Figure 4.9, while the right side panel focuses on the carbonyl region.

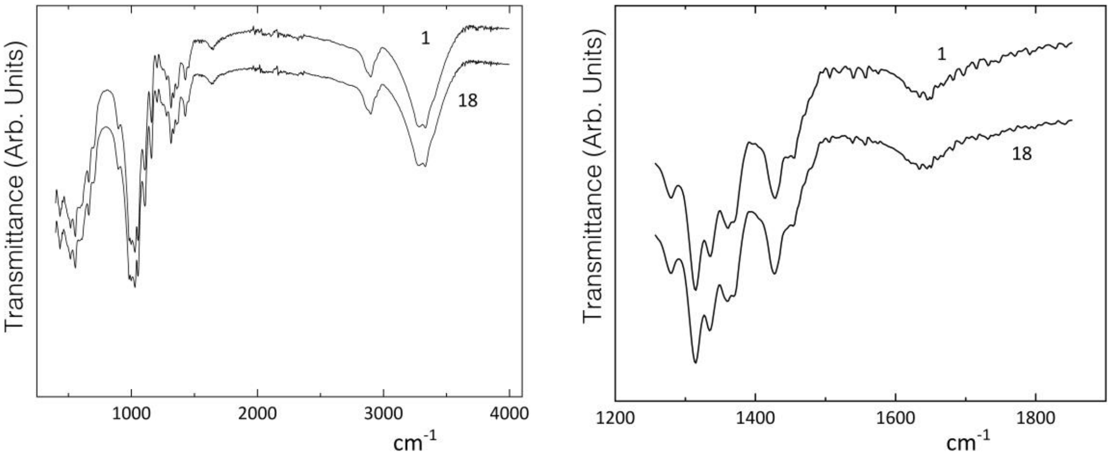

Figure 4.9. Left: FTIR spectra of sample 1 (blank) and 18 (irradiated at 10 kGy, thermally treated, 144-h aged). Right: focus on the region of the carbonyl groups for sample 1 (blank) and 18 (irradiated at 10 kGy, thermally treated, 144-h aged). Adapted from [56].

This finding is somewhat unexpected on the basis of the above described effects of γ-irradiation and ageing on colour changes, mainly ascribed to the formation of oxidised groups [76,77]. However, the presence of non-bonded water in paper can supply a possible explanation, not allowing an easy recognition of oxidised functions [52]. Indeed, the presence of O-H stretching from free water may mask changes in the carbonyl region [82].

4.4.5 Statistical analysis

The results of ANOVA analysis show that all the treatments and their interactions cause significant effects on tensile strength, while only γ-irradiation and ageing produce significant independent effects on tearing resistance.

As far as colour differences are concerned, each single treatment, including thermal drying, seems to cause significant statistical effects. In addition, given that also the interactions among the various treatments turned out to be significant, the effects of γ-irradiation within the groups ought to be evaluated. The effects of γ-irradiation on ΔE^*_{ab} result to be the same in the various reference groups, colour changes mainly increasing with increasing irradiation dose, as shown in Figure 4.7, where it can be noted that the ΔE^*_{ab} gap between the irradiated and non-irradiated samples increases with the extent of ageing.

4.5 Conclusions

Opposed opinions are reported in the literature on the suitability of γ-radiation treatments for paper disinfection, especially in connection with cultural heritage objects.

The effects on pure cellulose paper of γ-irradiation at two doses (i.e., 5 and 10 kGy), and two additional treatments (i.e., thermal drying and ageing for 24 and 144 h), were investigated by means of destructive (viscometry and mechanical tests) and non-destructive (FTIR spectroscopy, SEM and colorimetry) techniques.

The results point out a notable decrease of DP produced by the 5-kGy dose of γ-rays, the higher dose (i.e., 10 kGy) resulting in a much smaller additional reduction. Smaller effects on DP are also associated to thermal drying and ageing. On the contrary, γ-irradiation slightly affects colour. Colour changes were found to be hardly perceptible by the human eye, in terms of both the ΔE^*_{ab} and ΔE_{00} parameters, in the samples exposed only to γ-rays. In addition, in spite of the sizeable DP decrease, also the tearing resistance resulted to be only slightly affected by γ-irradiation, as well as by drying and ageing treatments. Likewise, drying and γ-irradiation do not produce considerable effects on tensile strength. A notable decrease of DP, accompanied by very small changes of mechanical properties, can be traced back to the fact that mechanical degradation accumulates randomly and independently of DP for paper with DP higher than 800, as reported in the literature.

As far as the controversy over the use of γ-radiations for paper disinfection is concerned, according to the present results, whilst a 5-kGy dose of γ-rays produces a sizeable decrease of DP, it barely affects physical properties such as colour, tensile strength and tearing resistance, at least until the final DP is not smaller than 800. Therefore, in light of these findings, it can be concluded that a 5-kGy γ-radiation, provided its effectiveness in disinfection, produces damages acceptable when compared to those occurring in case of no treatment, namely, when the alternative is no document at all. It seems thus reasonable that the possibility of using γ-irradiation should not be rejected *a priori*.

4.6 References

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