PHD THESIS SUMMARY

THE BEHAVIOUR OF SOME MATERIALS FROM CULTURAL AND ARCHIVES HERITAGE TO THE TREATMENT WITH IONIZING RADIATION

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Introduction

Bio-polymeric materials are of interest for industrial applications, especially in the context of the promotion of renewable resources and biodegradable materials. However, there is an area where bio-degradation is not desirable: the preservation of cultural heritage objects. Large quantities of objects, most of which based on the most common bio-polymers in nature (cellulose and collagen), are preserved and are intended to be kept as long as possible in museums, libraries, archives or other types of public or private collections. The age of an artifact or the information it contains gives it cultural, historical or even material value.

Accidents, natural calamities, pollution or simply negligence can endanger cultural heritage items, not only through physical and chemical aggression, but also by creating conditions for the development of biological attacks: bacteria, fungi or insects can completely destroy the organic material of the cultural heritage objects. Once emerged, the biological attack of large-scale collections is difficult to stop: microorganisms have the ability to maintain their own microclimate and to promote symbiotic relationships with other microorganisms or insects. In particular, the paper poses a lot of problems with its long-term preservation. Because the problems related to the preservation of large quantities of paper documents have not been resolved in an efficient way so far and because in many cases their condition is inevitably deteriorating, the treatment with ionizing radiation has returned to the attention of the conservators and resturators.

Ionizing radiation used in technological irradiation are of atomic nature (X-rays, accelerated electrons) or nuclear nature (γ rays), which can penetrate into large thicknesses of irradiated material but do not produce residual radioactivity therein. Because it is a physical treatment, irradiation with ionizing radiation does not pose problems with residues or persistent pollution. Ionizing radiation treatment has long been used in technological irradiation for the sterilization of medical and pharmaceutical materials, but has not enjoyed popularity in cultural heritage field due to question marks about collateral effects (aging or potentially destructive) that it can have on objects of cultural value. By definition, ionization is the characteristic phenomenon of ionizing radiation and is followed by the initiation of chemical, oxidative or radical propagation mechanisms (the biocidal effect, for example, is largely due to breakage of the double helix of the DNA molecule).

Due to the peculiarities of the interaction of ionizing radiation with cellulosic materials, the answer to the questions about the potential negative effects is not easy to give: the changes in the chemical and macromolecular structures at the relatively small doses of radiation, of interest for the treatment of cultural heritage objects, are at the limit of detection of the analytical methods. The studies carried out in this doctoral thesis aim at establishing the relevance of a set of analytical methods for investigating the properties of cellulosic materials and studying the irradiation effects on them, by establishing correlations between the properties of the material that are usually determined by destructive methods with high consumption of material (which is generally not available in cultural heritage objects) and properties determined by non-destructive or minimally invasive methods.

1. Cellulose and paper

Cellulose is the most common biopolymer in nature, has a relatively simple structure and is the main constituent of plant tissues. Its origin is why cellulose is naturally present in a wide variety of molecular masses and mixed with other compounds of plant origin (lignin, hemicellulose and other polysaccharides). Cellulose (1,4-β-glucan) is a linear syndiotactic homopolymer of D-anhydrogluco-pyranose. The bond between monomer units is β (1-4) - glycosidic (Fig. 1). Syndiotacticty leads to repeat of the cellobiose dimer, and cellulose can be considered an isotactic polymer of cellobiose. The conformational structure is given by the angle of the bonds in the monomer unit, by the length and torsion angle of the glycosidic bonds. The presence of intramolecular hydrogen bonds makes the structure of the cellulosic backbone most likely in the form of a spiral in a polar solvent [1].
The molecular structure of cellulose \( ([C_{6}H_{10}O_{5}]_{n}) \).

In realizing the works of the thesis, on interest there is cellulose in a natural state or a state close to it, and therefore its structure must be traced on 3 levels:
- molecular structure of the polymer chain;
- supramolecular packing and ordering of polymer chains;
- morphological level of cellulose fiber.

Hydrogen bonds are responsible for the supramolecular structure of cellulose. In addition, a great number of water binding possibilities are available, which can also create intermolecular bridges. The extensive network of hydrogen bonds is the one that greatly assures the macroscopic cohesion of the cellulosic material.

One of the supramolecular structures of cellulose, always present in cellulose of natural origin (confirmed by X-ray and MRI diffraction measurements), is type I crystalline cellulose (Figure 2a). Its abundance and stability is due to the energy minimum it offers. The percentage of crystalline phase for natural cellulose is relatively high (46% -63%) and is higher than that of reconstituted cellulose (11-45%) [1]. For the amorphous phase there is no well established model but its structure is closely related to the morphological level of cellulose of natural origin.

Cotton fibers have the highest cellulose content and their hemicellulose and pectin can be easily removed by simple procedures. Various other types of plant fibers (hemp, flax, sisal) also have high cellulose content, but it is usually preferred to use them as such in the textile industry, instead of pulping (cellulose separation). Wood has lower cellulose content but is cheaper and although lignin removal processes are complicated and more costly, wood remains the main source of industrial pulp [2].

One of the oldest uses of cellulosic material is that of support for the written information. Papyrus and wood tablets are of minimal processing of the natural material. The application of a physicochemical process of fiber separation and sheet forming, led to the obtaining of paper — historically dated in Sec. II a.c. in China. The secret of papermaking spread much later, first in the Arab world (7th century), and then in Europe, in Spain (9th century). Hand making of paper continued until the end of the 18th century, when the first attempts were made to continuously produce paper (Didot-1796, Fourdrinier-1801 [2]). The principles of the Fourdrinier machine have been preserved so far, and the paper production has grown in size after the introduction of pulp from wood in the middle of the XIX century. Regardless of the source of the raw material (cotton cloth or delignified wood fibers), the paper is obtained by a damp process in which cellulose fibers are initially dispersed.
and then interlaced into a sheet of the desired size. The ability of cellulose to form intermolecular hydrogen bonds allows the creation of the paper fiber network. The orientation of the fibers on handmade paper is completely random, but in continuous fabrication (Fourdrinier), because of the continuous motion of the web, the fibers in the cellulose paste are aligned with the direction of advancement of the web ("machine direction"). This alignment results in different paper properties in two perpendicular directions.

At present, depending on their use, which also leads to certain specific physicochemical characteristics, paper products can be classified as follows [3]: - Newsprint; - Coated and uncoated writing / printing paper; - Packaging paper; - Corrugated paper; - Absorbent paper; - Industrial and special papers; - Cardboard. Of interest to the topic of the thesis (paper found in archives, museums and libraries) are: - manual paper (without sizing additives or only with traditional additives of natural origin); - Whatman paper (study model for pure cellulose paper); - printed and uncoated writing / printing paper; - newspaper paper.

Over time, various additives have been introduced in papermaking to improve the manufacturing process or paper properties. Initially the additives were few and exclusively of natural origin, but at present their range has greatly diversified. The use of additives does not necessarily lead to better paper quality but contributes to the desired quality with the lowest cost and consumption of raw material. Noteworthy is the fact that much of these additives are only process additives that facilitate the dispersion and / or aggregation of cellulose fibers and fillers and only a small part are functional additives, which give certain properties to the paper [2]. Gypsum and starch were precursors to the use of starch glue as a sizing agent (arabic advanced method in VIIth Century). In Europe (9th-13th centuries) animal glue was introduced as sizing agent. Later (after 1800), the colophony sizing was introduced. Because it is responsible for the problems of acid paper, it has now been replaced with synthetic resins. With improved papermaking methods, an important factor has been to reduce the amount of raw material and reduce the thickness of the paper. The reverse of this reduction is the decrease in paper opacity. The problem has been solved by using materials that, in addition to increasing opacity, improve the degree of whiteness and paper weight. The most common fillers are clay (kaolin) and calcium carbonate, used together with other pigments: titanium dioxide, aluminum hydroxide and talc. Paper mechanical resistance is an important feature for its use (writing, printing, wrapping paper, etc.). Starch, the oldest additive used as a sizing agent, provides increased mechanical strength (various forms of modified starch are currently used). Other synthetic additives for increasing dry paper resistance are anionic and cationic derivatives of polyacrylamides.

The manual paper making process is simple and practically does not require process additives. In this case, it is possible to speak at most about the residues from the previous stages, preparing the "paste" of paper (bleaching, maceration, etc.). Along with switching to industrial manufacturing (Fourdrinier process), a multitude of additives for cellulose functionalisation and productivity increase [2] were gradually introduced:
- Flocculants which act by neutralizing the negative charges of the fillers or by forming molecular bridges.
- Dispersing agents that prevent flocculation.
- Drainage agents, regarding the reuse of reagents in the paper preparation solution.
- Antifoams (partially hydrophobic solids).
- Moist resistance enhancers.
- Step adjustment agents.
- Crepe agents (facilitates delamination after drying).
- Biocides (slimicides).

With the exception of fillers that can reach up to 30% of the paper weight, the other additives are used in very small quantities, a few percent of the final paper weight [2].

2. Effects of ionizing radiation on cellulose and paper

Ionizing radiation is that type of radiation that produces the ionization of atoms in the irradiated material. This definition takes into account the effect and not the nature of the radiation, so in the category of ionizing radiation, both ☢ - "nuclear" radiation and X - radiation "atomic" nature
come into play. In addition to electromagnetic radiation $\gamma$ and X, also in the category of ionizing radiation, accelerated electron beams are included, but UV radiation is not included. In fact, the term "ionizing radiation" has technical significance, and when it comes to "treatment with ionizing radiation" or "technological irradiation", it includes those radiation that have the primary ionizing effect, have a high penetration capacity and - important - do not produce nuclear reactions (radioactivity) in the irradiated material. Practical considerations make for a limited number of radiation options that can be used [5]:

- gamma ($\gamma$) radiation is an electromagnetic radiation, very penetrating, of nuclear nature. Of interest are the radiation from sources of Cobalt-60 radioactive isotopes and, to a lesser extent, Cesium-137.
- E-beam are electron that have been accelerated in an electromagnetic field to energies large enough to ensure good penetration of the irradiated material. To exclude the formation of radioactive isotopes in the irradiated material, a maximum energy limit of accelerated electrons has been set to 10MeV.
- X-rays (Rx) are electromagnetic radiation and their energy field overlaps with gamma radiation. Of interest for the treatment with ionizing radiation are bremsstrahlung X-rays that occurs when braking accelerated electrons in the electric field of the atoms of the irradiated target. For the same reasons as for accelerated electrons, maximum energy has been set to 5MeV for the use in the field of ionizing radiation treatments.

An intuitive representation of the relative positioning of ionizing radiation over other types of radiation is presented in Figure 3.

After the primary interactions (Figure 4), free electrons (photoelectrons, Compton electrons, electron-positron pairs) can suffer: - braking (inelastic splintering) through Coulombian interaction with the nucleus, which creates Bremsstrahlung photons; - collisions (elastic scattering) following Coulombian electron interaction in the electronic shell of the atom. The de-excitation of the atom or ion from the excited state takes place by rearranging electrons on atomic energy levels and is accompanied by the emission of photons with energies characteristic of each atomic system (characteristic X-ray). Electrons and photons resulting from primary interactions and de-excitation are called secondary radiation. Interaction of accelerated electrons with irradiated material is similar to that of secondary electrons resulting from interaction of gamma or X photons (braking, elastic collisions), except that in this case they start from higher energies (up to 10 MeV). Essentially, primary radiation loses energy when passing through irradiated material and this energy is absorbed by local energy transport (secondary radiation). Photons and electrons lose energy through successive interactions until their energy is completely absorbed or until they leave the irradiated material. With the decrease in photon and electron energy, a multitude of other excitement effects appear on various atomic and molecular energy levels. The de-excitation is radiation and there is always a thermal effect that dissipates part of the energy absorbed by the irradiated material.

![Figure 3 Energy range of ionizing radiation](image-url)
Figure 4 Primary interactions of photons and electrons with irradiated material: a) photoelectric effect; b) Compton effect; c) generation of electron-positron pairs; d) elastic scattering of the electrons; e) inelastic scattering of electrons.

If physical interaction can be described analytically or numerically, the subsequent chemical reactions will be as complex as the composition of the irradiated material. Radiation induced ionization is the triggering factor for getting out of equilibrium the chemical system. If the atom is part of a molecular structure, interaction can result in a separation of the molecule in ions with different polarities. The resulting free radicals are highly reactive chemical species and have a short lifetime, generating a succession of other reactions (degradation or synthesis), specific to the irradiated system. For complex systems (macromolecules, polymers), competing reactions may predominantly lead to splitting (e.g. depolymerisation of teflon) or crosslinking (intermolecular bond formation, in case of polyethylene, for example), specifically for each material and/or temperature and pressure conditions. Crystalline or semicrystalline structures have a more peculiar behavior: the crystalline structure is quite poorly affected, but free radicals can be immobilized for long periods of time. The release of these free radicals over time can produce changes that occur after irradiation and can be associated with the aging phenomenon.

3. Literature considerations on the treatment with ionizing radiation for cultural heritage on paper

Experiments performed since the 1950s have highlighted the fact that cellulose is degraded by ionizing radiation. In 1955, Charlesby establishes a relationship between the average molecular weight of irradiated cellulose and the absorbed dose, starting from the hypothesis of the random breakdown of the cellulose macromolecule chain, and taking into account the results obtained for other polymers [7]. Charlesby verified this relationship with the experimental data obtained from the accelerated cellular degradation of cotton and wood pulp and calculated a pulp degradation yield of 0.16% breakage of monomer units at $10^6$ Roentgen exposure (8.8 kGy). Later, Horio et al. [8] presented an empirical equation (independent of the molecular weight distribution of cellulose) that binds the degree of polymerization resulting from irradiation of the initial polymerization degree, the absorbed dose and the probability of breaking a β-glycosidic bond. Horio calculated a lower cellulose degradation value: 0.067% breakage of monomer unit linkages at an exposure of $10^6$ Roentgen (8.8 kGy). This corresponds to a radiochemical yield (number of broken links per 100 eV of energy absorbed) of $G = 4.8$. More recently, Bouchard et al (2006) [9] explains the correction of Charlesby’s model in terms of experimental data obtained also from accelerated electron irradiation. Bouchard found, based on more precise molecular weight distribution measurement, by SEC - size exclusion chromatography, that the molecular weight distribution for high dose irradiated cellulose was not exponential (as Charlesby assumed). Bouchard obtained the linear dependence between the number of breakages of the cellulosic polymer chain and the absorbed dose in the (20-240) kGy range, but also pointed out that the radiochemical yield for cellulosic breakage is different for different energies of the accelerated electrons. The values determined for the cellulose breakage probability were 0.093% for 1 kGy at 4.5MeV and 0.048% for 1 kGy at 10 MeV energy. In the same experiment, Bouchard highlighted a linear dependence between the number of breaks of the polymer chain and the elongation at zero span tensile test, in the dose range (20-240) kGy.

Molecular mass measurements (viscosity or SEC) of the above works refer to cellulose fiber cellulose macromolecules (made from cotton or wood) irradiated as such and then dissolved in the solvent. When dissolved in the solvent, however, the hydrogen bonds responsible for the macromolecular structure of the cellulose are lost.
First literature reports on the applicability of ionizing radiation treatment for cultural heritage objects included verification of the degradative effect of decreasing the average molecular weight of cellulose, for paper irradiated at the relatively high absorbed doses used for the sterilization of medical devices. Although other paper properties did not appear to be substantially affected (mechanical strength, whiteness [10]), the significant decrease in polymerisation does not recommend irradiation as a conservation treatment [10, 11]. Continuation of studies on the possibilities of application of radiation treatment for cultural heritage has been interrupted for a while due to the spread of the treatment with a fumigant gas, also borrowed from the field of medical sterilization (ethylene oxide) and the attempts to widespread application of other physical treatments (anoxia, freezing at low temperatures). Because the efficiency of classical, chemical or physical, biocidal treatments is still questionable [12], irradiation studies have recently been resumed, on a systematic basis, by research groups from several countries: Italy, Brazil, Argentina [13-32]. Some useful information on paper behaviour under irradiation was obtained in a more specific application: irradiation of correspondence in order to prevent bioterrorist attacks [33-39].

In the studies reported in the literature, besides the paper-specific testing methods (physical-mechanical, colorimetric, pH, permeability, viscometer, etc.), also modern investigation techniques were used (vibration spectroscopy, thermal and thermo-mechanical analysis, magnetic resonance spin or nuclear, X-ray diffraction, etc.), in an effort to obtain the most accurate results on the effect of irradiation in the dose range of interest for conservation treatments.

In Italy, a multi-year study, in a collaboration between ENEA - the Entity for New Technologies, Energy and the Environment, the Central Institute for Pathology of the Book, the Polygraphic Institute and the Italian National Printing Center, addressed the effects of irradiation on the two paper models (Whatman - pure cellulose paper and writing paper) through a multitude of analytical methods (mechanical tests, vibration spectroscopy, colorimetry, pH, Kappa index, medium polymerization degree) [13-24]. Much of the results obtained by the Italian group were published in the Restaurator (De Gruyter), one of the publications dedicated to the preservation and restoration of cultural heritage. The published results show that although at 10kGy the degree of polymerization drops to less than 50% of the initial value (non-irradiated), there was no evidence of alteration of other paper properties. One of the results was obtaining a license from the Italian Ministry of Culture to apply radiation treatment for the preservation of documents at doses lower than 5kGy [16]. Although not all authors recommend radiation treatment, the results show that irradiation no longer produces significant effects on cellulose degree of polymerisation in case of highly degraded paper, similar to the old paper from XVII century [20].

A series of studies conducted in Brazil [25-29] focused on the radiation resistance of fungi isolated from library books, as well as tests of mechanical and optical properties of reference papers, irradiated at 15kGy. The results show a more pronounced decrease of the zero-span resistance compared to other mechanical properties, suggesting that the fibers are more affected than the paper as a whole. The instrumental color variations are insensible to the naked eye.

Similar studies have been conducted in Argentina [30-32], and from their conclusions it is noted that the effect of accelerated aging is stronger than effect of irradiation. The optimal values for a minimal reduction of cellulose degree of polymerisation are less than 3kGy [32].

After the incident with Bacillus anthracis in USA (2001), several studies were published related to irradiation of mail and postal materials at very high doses (> 100kGy) in order to prevent bioterrorist attacks [33-39]. Although the doses are much higher than those required for the treatment of cultural heritage objects, the published results contain interesting conclusions about the effect of irradiation on the documents: - in a gas chromatographic study, volatile compounds similar to those from cellulose pyrolysis were found, suggesting a similarity of degradation mechanisms [37]; - Inks are not affected by irradiation, even at high doses [38]; - at 100 kGy the bending strength decreases with ~ 5% for magazine paper and ~ 15% for newspaper paper, but the results are strongly affected by the non-uniformity of the paper (its mass and thickness) [39].

A general conclusion that can be deduced from the studies published to date is that although the degree of polymerization is significantly reduced, for absorbed doses of up to 10 kGy, the collateral effects on other properties of the cellullosic materials are insignificant, within the limit of the statistical deviation or the uniformity of the material tested. Much of the results published until
2016 were reviewed in a publication of the International Atomic Energy Agency [40], which mentions the effects of irradiation on paper as side effects that are accepted when it comes to saving large quantities of documents that can not be treated efficiently and quickly enough by other methods.

4. Materials and methods

Taking into account the great variability of the existing paper types and the different state in which they appear in the field of cultural patrimony heritage (aging, physico-chemical or biological degraded), for the experimental studies in this thesis I used samples from a wide range of assortments and paper types: - pure cellulose materials (Whatman paper - present in most literature studies, hardwood and softwood pulps, cotton wool); - contemporary reference paper (2 kinds of copying paper - local and imported, 3 types of writing paper - chalk, ordinary and with watermark); - paper for offset and paper up to 110 years old (from archive collections, library or museum: 2 books published in Romania and 2 in France, 2 Romanian publications and 3 types of documents in the archive). The old manhand-made paper (XVI-XIXth century) was only available for non-destructive tests (FT-IR and FT-Raman).

Based on the literature survey on the possibility of obtaining new results, I selected the following analytical methods for the comparative characterization of the cellulosic material and the irradiation effects on it: simultaneous thermal analysis (thermogravimetry and differential scanning calorimetry), Fourier Transform vibrational spectroscopy: infrared (FT-IR) and Raman (FT-Raman), electronic spin resonance spectroscopy (RES), mass spectrometric gas chromatography (GC-MS), mechanical testing (tensile, penetration, bending) [41] and colorimetry in CIE coordinates (L * a * b *). Most of the tests were carried out with equipment from the laboratories of the IRASM Department of the National Institute for Research and Development for Physics and Nuclear Engineering, as well as equipment from Bucharest University (vibrational spectroscopy) and CEPROHART SA (mechanical testing). Samples from cellullosic, reference papers or old paper were irradiated with the SVST Co-60 irradiator and [39, 43] CG-5000 research irradiator of IRASM-IFIN-HH, in different irradiation geometries, in a high dose range (up to 100 kGy) - to highlight the suitability of analytical methods for determining irradiation effects. For the study of the interaction mechanisms at low dose irradiation, of practical interest for the paper preservation treatment, we have detailed the analytical studies on a narrower dose range (up to 30kGy) and at dose rates between 0.1kGy / h and 9.3kGy / h.

5. Physical and chemical characterization of non-irradiated paper

In a thermal analysis study (thermogravimetry and differential scanning calorimetry), we highlighted the differences between different types of cellulosic fibers and contemporary or old of paper. In Figure 5 we have been representing differential thermogravimetric (DTG) and differential scanning calorimetry (DSC) curves for some of the tested materials: pure cellulose, reference paper, and old paper. The curves in Figure 5 are represented in the temperature range of the endothermic thermal decomposition of cellulose for a constant heating rate of 10K/min under an inert (nitrogen) atmosphere, for sample mass of ~ 10mg. For comparison, each graph includes the curves for Whatman 42 paper. Figure 6 is summarizing the results obtained for selected three thermal parameters: mass loss, enthalpy variation and peak temperature at pulp decomposition for all 21 sample types tested.

The results presented in this chapter highlight the differences between different types of cellulose pulps and contemporary or old paper, such as:
- A slight asymmetry in the case of hardwood cellulose, which can be attributed to a higher content of small molecular chains (hemicelluloses). Asymmetry is more pronounced in the case of cotton wool, which has the appearance of two overlapped peaks. Apparently, one of the two fiber types of cotton wool has a higher thermal resistance than that of the Whatman 42 paper and, implicitly, a higher degree of polymerization.
- For the contemporary paper tested, the parameters of the cellulose thermal decomposition are in a relatively wide range, inferior to those obtained for Whatman paper. Watermark paper has a thermal decomposition very close to that of Whatman paper. One of the two assortments of offset paper has a pronounced asymmetry of the thermal decomposition peak, indicating the presence of two types of cellulose fibers.

- For three of the old book samples (1956, Annual Review of Physical Chemistry, 1956), the curves are similar to those obtained for Whatman paper, but the DSC peak parameters are smaller. Lower mass loss indicates lower cellulose content and the shift to lower thermal decomposition temperatures indicates a lower degree of cellulosic polymerization. It may come from a poorer initial quality of wood pulp and from its degradation over time. For the samples from the book published in 1976 two decomposition stages (two peaks in the DTG and DSC differential curves) were observed, probably due to the use of two types of cellulose fibers.

Mass loss at pulp decomposition (based on the total mass of dry matter - Figure 6a) provides information on the cellulose content of the paper. Thermal decomposition of pure cellulose in inert (nitrogen) atmosphere results in a char residue of about 20-30% at 350 °C, the mass of which decreases further with a slight slope as the temperature rises. Watermark paper has a similar mass loss of pure cellulose, indicating a low percentage of additives. Whatman 42 paper has the mass loss and thermal decomposition temperature of cellulose lower than Whatman 1CHR paper. This suggests a dependence of the mass loss and implicitly of the mass of the carbonated residue on the degree of cellulose polymerization: cellulose with a higher degree of polymerization has a higher thermal resistance but suffers a more advanced decomposition than cellulose with a lower degree of polymerization (lower char residue).

The enthalpy variance, ΔH (W / g), does not show a very good correlation with the mass loss for the cellulose decomposition zone: the presence of additives makes the paper assortments with a high content of filler and / or opacity additives (paper for copier, coated paper) have a lower value of the energy absorbed for the thermally decomposed cellulose mass unit. On the other hand, wood fibers have lower values of energy absorbed for the thermal decomposition than those obtained for old paper samples. This indicates the contribution of other factors to the thermal resistance of the paper than the degree of cellulose polymerization. The values obtained for older paper, higher than those for contemporary paper, suggest that there are other factors than the additives, usually present in a very small percentage (~ 1%), and which act on the cellulose fibers level and less at the level of the fibrils.
Figure 5 DSC and DTG curves for a) pure cellulose samples: hardwood and softwood cellulose, cotton wool and Whatman 42 paper; b) paper with watermark and two types of printing paper; c) Old book samples (Radioactivity, AS Sanielevici - RFLG-1956, Introduction to Physical Chemistry, IGMurgulescu - ICF-1976, Annual Review of Physical Chemistry, v7 - ANPC- 1976).

Generally, the DTG peak temperature is higher than the DSC peak (mass loss is recorded after energy absorption). Some of the cases analyzed are deviations from this rule (cotton wool) or a very small difference between the 2 peak peaks (1894 Calendar, watermark paper, CEPROHART copier Paper, Whatman 1CHR paper).

Table 1 shows the pyrolysis residues for thermal decomposition up to 600 °C (synthetic air: 50ml / min, 20K / min). It provides information on the content of inorganic additives (fillers, opacifiers and / or whitening additives) used in the respective paper assortments. It is noted that the pyrolysis residue for the pure cellulose samples is very small (1-3%) with the exception of softwood cellulose (6.6%). For print papers (books and publications), the pyrolysis residue is much higher (23-27%), except for the 1978 publication (newspaper type). A higher pyrolysis residue (27-31%) can be seen on the copier paper.

Table 1 Pyrolysis residue at 600 °C (synthetic Air: 50ml / min, 20K / min) for cellulose pulp, Whatman and copier paper, and papers from old publications.

<table>
<thead>
<tr>
<th>Proba</th>
<th>Reziduul de piroliza la 600°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardwood cellulose</td>
<td>1.3</td>
</tr>
<tr>
<td>Softwood cellulose</td>
<td>6.6</td>
</tr>
<tr>
<td>Cotton wool</td>
<td>2.9</td>
</tr>
<tr>
<td>WHATMAN 42</td>
<td>1.0</td>
</tr>
<tr>
<td>XEROX copy paper</td>
<td>27.1</td>
</tr>
<tr>
<td>CEPROHART copy paper</td>
<td>30.9</td>
</tr>
<tr>
<td>Radioactivitatea -1956</td>
<td>23.8</td>
</tr>
<tr>
<td>Annual Review of Physical Chemistry -1956</td>
<td>26.5</td>
</tr>
<tr>
<td>Annual Review of Physical Chemistry -1976</td>
<td>25.6</td>
</tr>
<tr>
<td>Introducere in Chimia Fizica -1976</td>
<td>25.0</td>
</tr>
<tr>
<td>Buletinul Oficial al RSR -1968</td>
<td>9.9</td>
</tr>
<tr>
<td>Calendar pentru toți romanii -1894</td>
<td>25.2</td>
</tr>
</tbody>
</table>
Several attempts are reported in the literature to establish a correlation between certain parameters of thermal degradation, the degree of cellulose polymerization and/or the age of cellulosic material [47-49]. In a similar way, it can be assumed that such a correlation can also be established in case of degradation induced by irradiation with ionizing radiation. We have found, however, that a number of factors make it difficult or impossible to establish a direct correlation:

- Thermal decomposition of the cellulose fiber blends produces partially superimposed peaks. Deconvolution is difficult when the fraction of a type of fiber is much smaller than the other and/or for a broad molecular mass distribution.
- The presence of irregularities in the DSC curves at the end of the thermal decomposition (processes of the carbonated residue) affects the accuracy of the peak temperature determination.
- The presence of large quantities of additives can delay the thermal decomposition process and shift the thermal decomposition peak to higher temperatures.
- The presence of endothermic DSC peaks in the 150-250 °C area, with no mass loss correspondent, indicates the presence of phase transition processes, which can also shift to higher temperatures the thermal decomposition peak of the pulp.
- The distribution of the molecular mass of cellulose, intrinsic and expanded due to factors contributing to the degradation of cellulose, contributes to the asymmetry and widening of thermal decomposition peaks.

In the vibrational spectroscopy study, we have verified that it can be used to confirm the presence and type of inorganic additives used in papermaking and for the identification of other components (additives). In Figure 7, there are representative FT-IR and FT-Raman spectra for four types of paper. The “fingerprint” area (1800-800) cm⁻¹ and CH stretch vibration area (3000-2800) cm⁻¹ [50,51] has a similar band structure due to the high cellulose content of the samples. Significant differences occur in the two copier paper samples by the distinct band of 1795 cm⁻¹, by the band from 1445 cm⁻¹ and the cleavage at 875 cm⁻¹, indicating the presence of calcium carbonate in a significant amount [52]. The absorption bands in the region (1400-1200) cm⁻¹ are due to the crystalline component of cellulose fibers. The ratio between the band area of (1372-1375) cm⁻¹ (CH bending) and the relatively constant band area of 2900 cm⁻¹ (CH stretch) is associated with the crystallinity factor (CF) and the ratio of 1429 cm⁻¹ (CH₂ scissoring) and the hydrogen bonding band of 898 cm⁻¹ is associated with the hydrogen bond strength [50, 51]. Another area of interest is that of the absorption band corresponding to adsorbed water (1750-1600) cm⁻¹ [51]. Two bands can be attributed to the carbonyl groups: the bands at 1733 cm⁻¹ (C = O stretch [51]) and 1601 cm⁻¹ [53]. They appear distinctly in the spectrum of the 1968 publication and in the form of "shoulders" in the spectra of other types of paper (more visible on copier paper than Whatman paper). The number of carbonyl groups is associated with the quality of cellulose used in papermaking and cellulose degradation (reduction of polymerization) over time or due to other degrading factors [51]. The age of the 1968 paper and the weaker quality of the used fibers (newspaper type) confirm this hypothesis. In the case of copying paper, the process of removing lignin from wood fibers causes cellulose macromolecule to break and induces a higher carbonyl content comparing to Whatman paper.

Figure 7 FT-IR reflection spectra (obtained with IR external probe) for five types of paper: Official Journal of RSR, I, no. 105-107, 1968, Whatman paper, XEROX copier paper, CEPROHART copier paper.
For IR spectroscopy also, attempts to correlate some parameters (the ratio of the intensity or area of specific bands) with the degree of cellulose polymerization [51] are reported. In this case the difficulties are given by:
- Overlaying bands interest with other bands of cellulose and / or additive bands. The deconvolution is difficult, especially in the case of old paper samples whose composition is not known or undergo major changes over time.
- Influence of the water absorbed in the sample, which also modifies (by superposition) the position and the spectral width of the bands of interest.

In the vibrational spectroscopy study we identified two areas of interest for studying the effect of irradiation on cellulosic material, which shows differences for the types of paper tested: the C = O vibration band (carbonyl groups) and the OH vibration band (intra and intermolecular).

6. Assessment of degradation induced by ionizing radiation for reference paper samples

The study for assessment of degradation induced by ionizing radiation was performed on reference paper samples. We used both thermal analysis and vibration spectroscopy as well as mechanical tests (traction, penetration, tearing, bending), colorimetry in CIE coordinates (L * a * b *), electronic spin resonance (RES) spectroscopy and gas chromatography with mass spectrometric detection (GC-MS). The irradiation of the samples was performed at IRASM irradiators in IFIH-HH over an extended range of absorbed doses (up to 100 kGy) and with dose rates of between 0.1kGy / h and 100kGy / h.

![Graph A](image1.png)

![Graph B](image2.png)

**Figure 8** The DTG peak temperature for thermal decomposition of cellulose according to the absorbed dose, (a) in oxidative atmosphere and (b) in inert atmosphere (10K / min, synthetic air and nitrogen, 40ml / min), for Whatman 42, hardwood and softwood pulp, and copier papers produced by CEPROHART and XEROX.

![Graph C](image3.png)

![Graph D](image4.png)

**Figure 9** Dependence on the absorbed dose for (a) DSC peak temperature and (b) DTG peak temperature for cellulose thermal decomposition (10K / min, inert atmosphere: nitrogen 40ml / min) for samples in RSR Official Journal 1968, Whatman, copying paper produced by CEPROHART SA and old paper from the Orthodox Christian Calendar (1894).
Figure 10 Dependence on the absorbed dose in the range (0-100) kGy for the maximum tensile force in (a) machine direction (MD) and (b) cross direction (CD). The error bars indicate the standard deviation for 10 specimens/test for copy paper and 5 specimens/Whatman paper.

Figure 11 Dependence of the mechanical properties of the absorbed dose in the range (0-15) kGy: (a) Maximum tensile strength in machine direction (MD) and (b) Bending strength, for 6 types of paper (two types of copier paper, Whatman 1CHR and two samples of old paper - Caiet from 1981, Form from 1984 and Official Journal of RSR from 1968).

Figures 8 and 9 show a part of the results obtained for the radiation induced changes in the thermal decomposition process for reference paper (0-100 kGy) and including old paper samples (0-15 kGy). Figures 10 and 11 show a part of the results obtained in testing the mechanical properties for the same dose ranges.

Parameters of the celulose decomposition peak have a uniform dose-dependence for doses higher than 25kG. In the range (0-10) kGy there is no uniform dependence on the absorbed dose for the thermal parameters [54]. For one of the copier papers (CEPROHART), there is even an apparent increase in the peak temperature. A similar behavior was obtained for most mechanical paper resistance parameters: a uniform dose dependence for doses higher than 25kGy, similar to all types of paper tested [54]. The decrease in tear resistance and penetration resistance is more pronounced for copier paper (made from wood pulp fibers and with high calcium carbonate content) than for Whatman (pure cellulose) paper. Considering that the reduction of the degree of cellulose polymerization is substantial at these doses [10, 17] and is higher when the degree of initial polymerization is higher [20], the decrease in mechanical strength should have been more important in the case of Whatman paper. The different experimental result suggests that other factors should be considered, in addition to the degree of cellulose polymerisation. Reducing the length of the cellulose macromolecule for Whatman paper is compensated by other aspects that contribute to the mechanical strength of the macromolecular assembly (e.g., hydrogen bonding structure). The decrease in tear strength is more pronounced for the copier paper subject to accelerated aging process. This can be explained by the fact that the supramolecular structure at the fibril level is altered by the synergistic action of temperature and water.
Some of the results we obtained in testing the radiation induced changes on paper color are shown in Figure 12. For comparison, we included the copier paper (CEPROHART) for which accelerated degradation treatment was applied (6 days at 80 °C and excessive humidity - 100% RH). In Figure 13 we presented the results obtained for white and opacity testing for reference paper and old paper, irradiated at doses up to 30kGy, at dose rates between 0.3kGy / h and 9.3kGy / h.

**Figure 12** Radiation induced color changes for three types of paper: Whatman 42, XEROX and CEPROHART copier paper in the (0-100) kGy range, expressed by CIE coordinates $L^*$ a* b*: a) Luminosity ($L^*$), red ($a^*$), c) blue / yellow coordinate ($b^*$).

**Figure 13** Radiation induced changes in optical properties of paper, for five types of paper (Whatman 1 CHR, XEROX, CEPROHART, RSR-1968 Official Journal, Form 1984) irradiated in the (0-25) kGy range at different dose rates: (a) White Index, (b) Opacity.

The change of brightness ($L^*$) is insignificant (<2 units, not observed by the naked eye) for all three types of paper, compared to the change caused by the accelerated degradation applied to CEPROHART paper (~ 10 units). The green / red index ($a^*$) shows a uniform drop (less red) of less than 2 units for both XEROX and CEPROHART paper. Because for Whatman paper this drop is not present, the decrease of $a^*$ parameter can be associated with the presence of calcium carbonate in the two types of copier paper. The non-uniform dependence of CEPROHART aged paper confirms this hypothesis: the color centers excited by the ionizing radiation in the crystalline structure of calcium carbonate are de-excited by the heat treatment. The stability of color centers additionally induced by high dose irradiation is less than that of those induced by low dose irradiation. The $b^*$ value (blue / yellow coordinate) increases evenly with the absorbed dose for all papers tested (more yellow and less blue), which creates the yellowish appearance of the paper at very high doses.

The white index and brightness decrease for all tested samples over the entire absorbed dose range analyzed. The lower decrease of these parameters in the Whatman paper indicates a greater contribution of irradiation induced modifications to calcium carbonate than that of cellulose-induced changes. The absence of returning these parameters to higher values after the accelerated degradation treatment (CEPROHART paper) indicates a greater stability of changes induced by ionizing radiation on calcium carbonate than those induced on cellulose. The changes induced by the accelerated degradation treatment (for non-irradiated CEPROHART paper) are higher than those induced by irradiation at 100kGy.
In Figure 14 are presented typical FT-IR and FT-Raman spectra for Whatman and copier paper. Differences between the vibrational spectra of irradiated and non-irradiated paper are small. In FT-IR spectra, the differences occur mainly with respect to the unsaturated C = O bonds, identified by the "shoulder" at 1730 cm$^{-1}$. Narrow band of 1796 cm$^{-1}$, assigned to the calcium carbonate [52] found in large quantities in the composition of the paper copier, also has a variation. However, this may be due to the overlapping with the wide band of water absorbed (1640 cm$^{-1}$) or to non-uniformity of distribution of calcium carbonate. The presence of the bands at 1603 cm$^{-1}$ in the Raman spectrum of copy paper can be assigned of aromatic rings, indicating the presence of lignin [55], and the band at 713 cm$^{-1}$ confirms the presence of calcium carbonate.

The crystallinity factor, calculated as the ratio of bands (1372-1375) cm$^{-1}$ and 2900 cm$^{-1}$ (Figure 15a), does not show a definite dependence on the absorbed dose. This shows that the significant reduction in the degree of polymerization does not have a direct consequence of crystallinity factor. Band area from 1730 cm$^{-1}$ (assigned to carbonyl groups - Figure 15 b) shows however an uniform dependence by increasing the dose absorbed, quasi-linear for doses higher than 25kGy, similar for the materials from pure cellulose and for the two types of paper copier. The results obtained confirm the results reported in the literature for cotton cellulose (Whatman paper) [51, 55].

**Figure 14** (a) FT-IR spectra in the range (850-3000) cm$^{-1}$ (64 scans, KBr pellet with 1 mg sample for 300 mg of KBr) and (b) FT-Raman spectra (3500-250) cm$^{-1}$ (1064 nm laser at 100mW, 100 scans per sample), for samples of Whatman and copier paper, in the range (0-100) kGy.

**Figure 15** Crystallinity index (a) and area of carbonyl band (b) for hardwood and softwood cellulose, Whatman 42, CEPROHART and XEROX copier paper.
The intensity of the central ESR signal (Figure 16) is not saturated up to 100kGy. The intensity for Whatman paper (pure cellulose) is higher than that for wood (hardwood or softwood) cellulose and copier paper, due to the higher content of crystalline cellulose. This result is in agreement with the values calculated for the crystallinity factor (Figure 14 a). It is noticeable the high intensity of the central ESR signal for softwood cellulose, much higher than the cellulose of hardwood and close to those obtained for cotton wool and Whatman paper. For the copier paper, the ESR signal is distorted by the presence of calcium carbonate. The decrease of ESR signal due to the release of trapped residues over time is faster in the first weeks after irradiation, and the ESR signal becomes almost stable after 4 weeks. This indicates a possible continuation (latency) of the structural and chemical changes of pulp after irradiation, which should be taken into consideration during the post-irradiation tests.

**Figure 16** The intensity of the central ESR signal, immediately after irradiation, for: hardwood cellulose, softwood cellulose, CEPROHART copying paper, cotton wool, and Whatman paper.

The HS / TD / GC / MS analysis of XEROX copier paper show the same volatile organic compounds reported in the literature [37]. The dose dependence for most volatile organic compounds is non-uniform. The volatile compounds with an increasing dependence on the absorbed dose (Figure 17) are: 11: pentane; 21: formic acid isopropyl ester; 30: tetrahydrofuran; 58: decane; 64: undecan 66; 67: 1-dodecene; 68: dodecane; 69: decanal; 71: undecanal.

**Figure 17** Dose dependence for the concentration of volatile organic compounds resulting from irradiation of Xerox copier paper.
For the degradation kinetics study, we chosen a lower grade paper, from an archive, older than 40 years (Official Journal of the Socialist Republic of Romania, No. 105-107 / 1968). To decrease the interference of the adsorbed water in the paper samples, the samples were subjected to a dehydration cycle by heating up to 120 ° C. Activation energy was estimated in two ways: a) using the Kissinger equation - for 4 thermal decomposition rates: 2 K / min, 5 K / min, 10 K / min and 20 K / min (Ea\textsubscript{DSC}) and b) by the energy at 50% isoconversion (Ea\textsubscript{DTG}). The results are graphically represented in Figure 18. The differences obtained for the activation energy calculated by the two methods suggest the existence of processes (transitions) without loss of mass at the thermal decomposition of paper, that can be attributed to the hydrogen bonds that “support” the complex macromolecular system of the paper. The non-uniform dependence on the absorbed dose of the studied parameters is due to the non-uniformity of between the 6 bundles of paper in the BO RSR-1968.

The content of carbonyl and carboxyl groups does not directly affect the mechanical (macroscopic) properties of paper, but their presence is assumed to be an indication of paper durability (aging resistance) [10, 20, 51]: carbonyl and carboxyl groups in the chain macromolecular of cellulose are hot spots for subsequent degradative reactions. Experiments from the literature shows a concentration of carboxyl groups induced by irradiation much lower than that of carbonyl groups [51] and the study we made only refers to the evaluation of the latter. In addition to the classical (chemical) determination of carbonyl content [20], vibrational spectroscopy offers a minimally invasive (ATR) or non-invasive (external probe) alternative for determining them. We processed the FT-IR spectra by a method similar to that described in [51], by subtracting the FT-IR curve corresponding to the non-irradiated sample from the FT-IR curve of the irradiated samples. Unlike [51], in order to eliminate the effect induced by the variation of the amount of water absorbed in the sample and other bands that interfere with the region of the absorbed water band, we applied a deconvolution technique before subtracting the curves. On Whatman paper, we obtained only 2 bands, partially overlapped, of which one corresponds to C = O stretch vibrations by the process described above. For the other types of samples, we obtained several peaks (probably from impurities or additives in the case of copier paper) but in all deconvoluted spectra the band at ~1740 cm\(^{-1}\), corresponding to the carbonyl groups, is present.

In Figure 19 is shown the dose dependence of the carbonyl band area, fitted with the function proposed by Baccaro for Whatman paper [51]. The results we obtained for pure cellulose materials (Whatman paper and cellulose fibers from hardwood or resinous wood) are in line with those reported by Baccaro (parameter b = 0.8). On copier paper, we found a slower increase in the IR absorption band area of the carbonyl groups. This may be correlated with the higher number of carbonyl groups present in unirradiated samples, which means less availability for the formation of new carbonyl groups, or with the presence of additives that have an inhibiting role for oxidation.

Figure 18 Dependence of the thermal decomposition kinetics on the absorbed dose for samples from the RSR - 1968 Official Journal: a) Activation energy calculated by the Kissinger method (at 4 heating rates: 2 K / min, 5 K / min, 10 K / min and 20 K / min), b) Activation energy calculated from DTG data at isoconversion rate of 50%.
Figure 19 Evolution of carbonyl content for samples of Whatman paper, copier paper (CEPROHART and XEROX) and hardwood and softwood pulp, in the (0-100) kGy dose range.

7. Study of hydrogen bonding in paper pulp by thermogravimetry and differential scanning calorimetry

The results of the experiments presented in chapter 6 confirm the results obtained by other research groups regarding the lack of correlation between the relatively high decrease of the degree of cellulose polymerization and the reduced decrease of the macroscopic properties of the irradiated paper, at doses lower than 10kGy. In chapter 5 we highlighted a series of limitations that may affect the finding of a direct correlation between the resistance to thermal decomposition or FT-IR parameters and the degree of cellulose polymerization. The differences obtained for the activation energy calculated by the Kissinger method and the 50% isoconversion energy suggest that there are processes without loss of mass at the thermal decomposition of the paper, which may be associated to the macromolecular structure of paper: dissociation of the hydrogen bonds.

Hydrogen bonds are the basis of the supramolecular structure of cellulose and the three-dimensional fiber network constituting paper [1] and contribute to the thermal stability of cellulosic material for an important temperature range. The glass transition of amorphous cellulose was studied by differential scanning calorimetry [56-60], thermo-mechanical analysis [61] or numerical simulation [62]. Transition of the glass transition temperature from temperatures below 100 °C to temperatures above 200 °C was reported when the water was extracted from the cellulosic material.

Thermal analysis tests were performed first on Whatman 1CHR [63] (pure cellulose paper, chromatography grade). To reduce the influence of water absorbed on paper, we conditioned the samples for 24 hours at 5% RH at room temperature in a desiccators with the calcium chloride. Each test was performed in triplicate. For the DSC curves analysis we used a peak separation (deconvolution) technique included in the Netzch analyzer software package.

In Figure 20 are shown the typical thermograms obtained at the thermal decomposition of Whatman paper, in (0-30) kGy dose range. Water loss (I) is visible in the DSC curves, but is not present in the DTG curves due to the preliminary dehydration of the samples. The values above 100 °C of the DSC peak temperature indicate the majority contribution of bondend water [56,64-66]. In the region marked with (II), a similar profile for the DSC curves is observed, regardless of the absorbed dose, with no mass loss correspondence in the DTG. Such a profile has been associated with the literature with depolimerisation of cellulose ("aging peak" [58, 61]) or to a glass transition [56, 59]. Such peak is mentioned in the literature around the temperature of 60 °C [58] but it was also observed around the temperature of 250 °C [67, 68]. Region (III) shows the profile of the thermal decomposition of cellulose. The endoderm peak is found at a relatively high temperature due to the high molecular

\[ y = a \cdot x^b \]

<table>
<thead>
<tr>
<th>Material</th>
<th>b</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whatman paper</td>
<td>0.77</td>
<td>0.999</td>
</tr>
<tr>
<td>CEPROHART copier paper</td>
<td>0.68</td>
<td>0.983</td>
</tr>
<tr>
<td>XEROX copier paper</td>
<td>0.66</td>
<td>0.952</td>
</tr>
<tr>
<td>Hardwood pulp</td>
<td>0.81</td>
<td>0.978</td>
</tr>
<tr>
<td>Softwood pulp</td>
<td>0.85</td>
<td>0.980</td>
</tr>
</tbody>
</table>
weight (high degree of polymerization) of cotton cellulose. Taking into account the reduced sensitivity of DSC to temperatures above 400 °C and the random presence of changes in the differential scanning calorimetry curve, this region was not considered in the analysis below.

Figure 20 Thermo-gravimetric and calorimetric characterization of the thermal decomposition of Whatman 1CHR paper (nitrogen atmosphere: 40ml / min, heating rate 10K / min, sample weight ~ 10mg) irradiated in the (0-30) kGy range: a) DTG and b) DSC.

New information on changes induced by irradiation with ionizing radiation on the structure of the hydrogen bonding of paper pulp we obtained by the deconvolution of the peaks from the calorimetric curves. In Figure 21, DSC peaks are deconvolved in the approximation of a linear baseline between the start of the water peak and the cellulose decomposition peak endpoint: non-linear regression with the weight w = 1 for 3 asymmetric Gaussian peaks. All deconvolutions were obtained with a correlation coefficient better than 0.99918.

Figure 21 Deconvolution of peaks from the differential scanning calorimetry curve for Whatman paper: a) 0kGy, b) 28.20 kGy
Figure 22 The main parameters of the deconvolved peaks from the differential scanning calorimetry curves: a) temperature parameters, b) peak amplitude, c) peak half-width, d peak area.

For doses higher than 10kGy, an uniform dose dependence is observed, but for doses less than 10kGy there is no well-defined trend. Due to the reduction of the water loss by the preliminary dehydration of samples, there is virtually no overlapping of the first two peaks. Overlapping of peaks 2 and 3 increases as the absorbed dose increases. Upon increasing the absorbed dose, a shift towards higher peak temperatures of peak 2 and a shift to lower peak temperatures is observed. The shift to higher temperatures of peak 2 suggests a greater resistance of the hydrogen bonding assembly to rupture under the action of temperature. The shift to lower temperatures of peak 3 (thermal decomposition of cellulose) can be associated with the decrease in the degree of cellulose polymerisation. Following irradiation, a stronger hydrogen bonding structure delays the depolymerization of cellulose. For further breaks of cellulose macromolecules, a change in hydrogen bonds is expected: formation of new extra- and intramolecular hydrogen bonds and / or strengthening of existing ones (decrease of interatomic distance), leading (by cross-linking) to a global strengthening of the three-dimensional structure of intermolecular hydrogen bonds.

In the case of cellulose, there is no common and clearly defined concept in the literature on the assignment of IR absorption bands in the (3700-3000) cm\(^{-1}\) (OH stretch) region. Descriptions of this region include the deconvolution of bands that are not directly identifiable in the original data [71]. The data obtained for the crystalline component of natural cellulose (I\(\alpha\) and / or I\(\beta\)) correlated with the cellulose crystallography models and data obtained by numerical modelling, allow a generic allocation of the bands in the 3230-3310 cm\(^{-1}\) area for vibration of the inter-molecular O(6)H \(\cdots\) O(3) bonds. The bands in the 3340-3375 cm\(^{-1}\) area can be assigned to the intramolecular bond O(3)H \(\cdots\) O(5) and the bands in the 3410-3460 cm\(^{-1}\) area can be attributed to the intramolecular bond O(2)H \(\cdots\) O(6) [72, 73]. Cellulose amorphous regions also have intra- and intermolecular hydrogen bonds and may contribute to widening the bands attributed to the crystalline component [74]. In order to identify and highlight the separate contribution of these three types of hydrogen bonds, we applied a deconvolution technique (symmetric gaussian peaks) on the (3700-3000) cm\(^{-1}\) range. Figure 23 illustrates examples of Whatman paper deconvolved FT-IR spectra.

There are no major differences in the structure of deconvolved bands between non-irradiated and irradiated samples. For Whatman paper, besides the three peaks attributed according to the literature, we also obtained two smaller peaks (at 3295 cm\(^{-1}\) and 3385-3390 cm\(^{-1}\)) respectively, which may be assigned to intermolecular bonds, respectively intramolecular from the amorphous area. On copier paper, the deconvolution did not reveal a distinct peak in the (3375-3410) cm\(^{-1}\) area, and the assignment of the deconvoluted peaks was similar to those obtained on Whatman paper: the peak at 3290 cm\(^{-1}\) and 3305 cm\(^{-1}\) we have been attributed to the intermolecular O(6)H \(\cdots\) O(3) (with the smaller peak at 3295-3305 cm\(^{-1}\) for other intermolecular bonds), the relatively small peak from (3370-3375) cm\(^{-1}\) we assigned to the intramolecular bonds O(3)H \(\cdots\) O(5) and the wide and high peak from (3465-3480) cm\(^{-1}\) attributed to the intramolecular bonds O(2)H \(\cdots\) O(6). For both types of copier paper, deconvolution also resulted in a relatively high (3575-3580) cm\(^{-1}\) that could come from water vibrations related to the paper additive or other hydrogen bonds created by them.
In Figure 24, is shown the dose dependence for the position of the hydrogen bonding peaks, for all three types of paper tested. Peaks corresponding to inter- and intramolecular hydrogen bonds on Whatman paper are positioned at lower wavelengths (higher bond energy). This may be due to the better quality of cotton cellulose (higher degree of polymerization and crystallinity index) than cellulose made from wood. The proportion of intermolecular bonds (the ratio between the area of intermolecular bonds and the total area of the unconvolved peak) is higher for the two copier papers, which explains their better mechanical strength. For Whatman paper, at doses lower than 10kGy, there is a slight shift toward smaller wavelengths of the hydrogen bonding peak, corresponding to higher binding energies, consistent with observations on the strengthening of the hydrogen bonds structure from the thermal analysis study. Dose dependencies for copier papers (similar for the two types of paper) indicate a shift first to higher wavelengths (weakening of the hydrogen bonding structure) followed by a shift to smaller wavelengths, so that, at the end of the tested dose range, the position of the peaks is similar to that of non-irradiated samples.

As can be seen from Figures 25, 26 and 27, the influence of the dose rate in the range (0.1-4.3 kGy) is insignificant for all three types of paper tested, both in terms of thermal decomposition parameters and regarding the evolution of carbonyl groups and effect on hydrogen bonds evaluated by FT-IR spectroscopy.

**Figure 24** Dose dependence of the position of the peaks assigned to hydrogen bonds, for three types of paper (Whatman, CEPROHART and XEROX): a) intermolecular bonds O(6)H⋯O(3), b) intramolecular bonds O(3)H⋯O(5) and c) intramolecular bonds O(2)H⋯O(6).
Figure 25 Dose dependence of (a) end temperature of DTG cellulose decomposition peak and (b) for the DSC peak temperature corresponding to hydrogen bond decomposition, for samples of Whatman 42 and XEROX paper, unirradiated and irradiated at doses lower than 20 kGy anf for the dose rates of 0.1 kGy/h and 4.3 kGy/h.

Figure 26 Dose dependence of the peak area corresponding to the C = O (carbonyl) stretch vibration bands, at three dose rates (0.1 kGy/h, 1.1 kGy/h and 4.3 kGy/h), for Whatman (a), XEROX Copier Paper (b), and CEPROHART Copier Paper (c).

Figure 27 Dose dependence of the band position corresponding to inter-and intramolecular hydrogen bonds, at three dose rates (0.1kGy/h, 1.1kGy/h and 4.3kGy/h) for (a) Whatman and (b) XEROX Copier Paper (b).

The correlation between the mechanical properties of irradiated paper and the thermal analysis parameters is relatively easy be done for doses higher than 25kGy, given their uniform quasi-linear decrease on irradiation (Figures 8 and 10). The uncertainty of measurement is better for the thermal parameter, both because of the analytical method and because of the better uniformity of the samples used for thermal analysis (paper discs with a diameter of 5.5 mm) compared to the tests for mechanical properties testing (with larger dimensions 10 cm²). For these reasons, thermal analysis offers a better sensitivity to the study of changes induced by irradiation with ionizing radiation. A good correlation was obtained between the elongation at break and the activation
energy determined in the kinetic study. In Figure 28, the dose dependence of the breaking strength and the activation energy calculated from the thermogravimetry curves is compared to the activation energy (50% isoconversion). The "mirror" profile of the dependence of activation energy on the absorbed dose against that of elongation at break (with negative coordinates in Figure 28) is observed. Taking into account that the mechanical strength of the paper is mainly given by the hydrogen bonds, it can be concluded that the presence of hydrogen bonds influences the thermal decomposition process of paper pulp. Thus, a more rigid system (with higher mechanical strength) has lower thermal decomposition activation energy.

![Figure 28](image)

**Figure 28** Dose dependence for elongation at break and activation energy (50% isoconversion), in the (0-15) kGy dose range, for samples in the RSR Official Journal - 1968.

8. Ionizing radiation treatment experiments for disinfecting cultural heritage materials on cellulosic support at IRASM gamma irradiation from IFIN-HH

In a treatment experiment for old religious books we evaluated the changes induced by ionizing radiation treatment, by FT-IR and FT-Raman vibrational spectroscopy, in a non-destructive way, by using external non-contact probes. The books under study were treated by gamma irradiation after restoration but showed the traces of a very aggressive biological attack of woodworms. The books, belonging to a particular collection, are from the sec. XI-XIX: Origenes Adamati, XVIth century, Cazanie, sec XVII, Gospel, 18th-19th century, Pateric, 19th century.

![Figure 29](image)

**Figure 29** Biological attack of woodworms on old religious books.

In the IR spectra of the old paper, no changes are noted that reveal structural changes of it after irradiation with ionizing radiation. The shape of the IR spectrum for the restauration paper is different, in the (1100-1200) cm\(^{-1}\) area, pointing out that it is not structurally identical to the original paper. Modification of Raman bands' intensity at 3248 cm\(^{-1}\) and 778 cm\(^{-1}\) for irradiated paper can be
attributed to color change, but also to the high unevenness of the sample. From the IR and Raman spectra performed on the leather covers of the old religious books (XIV-XIXth century) structural changes can be observed in the irradiated samples regarding the increase or decrease of the intensity of the bands in the area (1750-1500) cm\(^{-1}\) and the area (900-1000) cm\(^{-1}\). The variations in the (1100-1800) cm\(^{-1}\) area are due to the high surface irregularity of the skin samples.

Figure 30 IR and Raman Spectra (500mW) for ORIGINES ADAMATI VOL I Section XVI, before and after irradiation, multiple points: PAG X P1 irradiated / unirradiated; PAG X P2 irradiated / unirradiated; PAG X P3 irradiated / non-irradiated (Japanese restoration paper); PAG XX P1 irradiated / unirradiated; PAG XX P2 irradiated / unirradiated; PAG XX P3 irradiated / unirradiated

Other recent experiments of ionizing radiation treatment performed at IRASM irradiator from IFIN-HH include [75, 76]:

- Collection of documents of D. P. Perpessicius Memorial House, belonging to the Brăila Museum. The deposit contains 15,239 books; 464 photos; 2573 periodic; 5970 manuscript files, of which 50 books before 1850; 9,000 books between 1850-1900; 6,189 books from 1900 to the present. Their degradation is due to improper conditions in the memorial house (lack of ventilation and heating, plank floor without any insulation). The contamination of the documents was primarily microbiological (fungi) but also with insects.

- "Official Journal" collection belonging to the Chamber of Deputies archive. The collection contains the legislative documents of Romania starting with the end of the 19th century (~ 20m\(^3\) of documents). Due to the improper storage conditions, along with its move to various locations until it was brought to Parliament’s current premises, the collection underwent a massive fungal attack (Figure 32). With the irradiation treatment for fungal decontamination (2014), non-destructive tests to monitor the effect of treatment were also performed at the IFIN-HH IRASM department.

- Collection of the Bucharest National Theater Museum. The collection contains old documents (books, scripts, manuscripts, photo albums) as well as paintings, costumes and other props. The collection suffered a major accident, being completely flooded during the 1978 fire, and was totally neglected, kept in bags, in insalubring basements, from 1978 until completion of the complete renovation of the Bucharest National Theater building in 2015.

- The Royal Patent Collection from the State Office for Inventions and Trademarks (OSIM) was hidden during the communist period in order to be saved from melting during the time when all the documents bearing the royal insignia were destroyed. After 1989, OSIM experts made efforts to rehabilitate the collection and return it to the public consultation circuit, but fungal contamination could not be effectively eliminated.

- Archive "SAHIA Film". At the direct request of the Ministry of Culture, the Sahia Film Archive was included in the IRASM ionization radiation treatment program. The archive, considered lost, was rediscovered in 2016, in a deplorable state (figure 33), in a totally improper basement. The treatment was performed at IRASM during 2016-2017, for ~ 50m\(^3\) of documents.
Final conclusions

The cellulosic materials are present in different forms in the cultural heritage objects. Of interest to the subject of the thesis, due to the particular problems for their treatment with ionizing radiation, are the materials in which the cellulosic fibers are processed in the form of paper.

In the studies reported in the literature, besides the paper-specific testing methods (physical-mechanical, colorimetric, pH, permeability, viscometry, etc.), other modern testing methods were used (vibrational spectroscopy, steric exclusion chromatography, thermo-mechanical, magnetic spin or nuclear resonance, X-ray diffraction, etc.) in an effort to obtain as precise results as possible on the effect of irradiation in the dose range of interest for cultural heritage conservation treatments. A general conclusion of the studies published to date is that although the degree of polymerization is significantly reduced, for absorbed doses of up to 10 kGy, the collateral effects on other properties of the cellulosic materials are low, within the limit of the statistical deviation or the uniformity of the material tested.

In the thermal analysis study for characterization of non-irradiated cellulosic materials (thermogravimetry and differential scanning calorimetry), we highlighted the differences between different types of cellulosic fibers and contemporary or old assortments of paper. We have found that a number of factors make it difficult or impossible to establish a direct correlation between the thermal decomposition parameters and the degree of cellulose polymerization. In the vibrational spectroscopy study, we have verified that this method can be used to confirm the presence and type of inorganic additives used in papermaking and the identification of other paper components (additives). In this case also, the correlation of some parameters (ratios of the intensity or range of specific bands) with the degree of cellulose polymerization is difficult. We have identified two areas of interest for studying the effect of irradiation on cellulosic material, which have differences for the...
types of paper tested: the C = O vibration band (carbonyl groups) and the OH vibration band (intra- and intermolecular hydrogen bonds).

In the studies of radiation induced degradation for reference paper samples, we included more types of paper than those in the literature and we used several methods of analysis:

- The results of the thermal analysis confirm that the parameters of the pulp decomposition peak of the cellulose have a uniform dependence on the absorbed dose for doses higher than 25kGy but in the range (0-10) kGy there is no visible dependence on the absorbed dose.
- We have obtained the same confirmation for the mechanical properties of paper: mechanical strength parameters have a uniform dependence on the absorbed dose only for doses larger than 25kGy, not for the low dose range.
- We have highlighted the possibilities of correlating some mechanical parameters with pulp decomposition parameters: tensile, tear or penetration resistance, and endothermic DSC peak for thermal decomposition of cellulose under an inert nitrogen atmosphere, or DTG peak temperature. The lower measurement uncertainty and the better uniformity of the samples used for thermal analysis suggest that this may be substituted for some mechanical tests to study the effect of irradiation with ionizing radiation on the macromolecular structure of cellulose.
- The results we have obtained in testing radiation induced changes on paper color show that: changes induced by thermal degradation treatments of unirradiated paper are greater than those induced by irradiation at 100kGy; the white index and brightness decrease is shown for all tested samples over the entire absorbed dose range. The lower decrease of these parameters in the Whatman paper indicates a greater contribution of irradiation induced modifications to calcium carbonate than that of cellulose-induced changes. For doses smaller than 10kGy, color changes are undetectable with the naked eye (total color difference is less than 2 CIE units).
- In the vibrational spectroscopy study we obtained confirmation of some literature results (for Whatman paper) for other types of paper and cellulosic material (copying paper and cellulose from hardwood and resinous wood). The crystallinity factor calculated as the ratio of the bands at \((1372-1375) \text{ cm}^{-1}\) and \(2900 \text{ cm}^{-1}\) has irregular variations and does not show a definite dependence on the absorbed dose (the reduction of the polymerization degree does not have a direct consequence to the crystallinity index). The area of of \(1730 \text{ cm}^{-1}\) band (concentration of carbonyl groups), however, has an increasing quasi-linear behaviour for doses higher than 25 kGy, similarly for pure cellulose materials (Whatman paper, hardwood and resinous cellulose fibers), respectively for the two types of copier paper being tested.
- The intensity of the central electronic resonance resonance signal (RES) shows a dose-dependent increase over the entire dose range studied (0-100kGy). The absence of the saturation phenomenon (expected for crystalline structures) can be explained by the fact that although the crystallinity index does not exhibit a clear dependence on the absorbed dose, the macromolecular structure of the cellulose changes as the absorbed dose increases.
- The HS / TD / cGC / MS analysis of XEROX copier paper highlighted the same volatile organic compounds reported in the literature. Generally, the concentration of volatile organic compounds increases non-linearly with the absorbed dose (a small number of compounds have an increasing dependence). Although irradiation has produced a series of volatile organic compounds that also identify cell degradation by accelerated aging (markers of degradation), their dependence on the absorbed dose is not uniform. This suggests changing the predominant response channels with increasing the absorbed dose.

In the degradation kinetics study, we obtained the dependence of activation energy, calculated by two methods, on the absorbed dose on a dose range of up to 30 kGy. The differences obtained for the activation energy calculated by the two methods suggest that there are processes (transitions) without loss of mass at the thermal decomposition of paper that can be attributed to the hydrogen bonds that "support" the complex macromolecular complex of the paper. The non-uniform dependence on the absorbed dose of the studied parameters is due to the inconsistency between the 6 bundles in the study published in 1968.

The content of carbonyl and carboxyl groups does not directly affect the mechanical (macroscopic) properties of the paper, but their presence is assumed to be an indication of a
decrease in paper durability (decrease in aging resistance). It is assumed that the position of the carbonyl and carboxyl groups in the macromolecular chain of pulp represents weakpoints for subsequent degradative reactions. Dependence on the absorbed dose of carbonyl content allows the paper to be distinguished from pure cellulose to modern high-additive paper. Fourier transform infrared spectroscopy allows the non-destructive evaluation (important for old documents) of the increase in the number of carbonyl groups following irradiation. For the absorbed water content, it was not possible to establish a univocal dependence on the absorbed dose. For pure cellulose samples the results obtained are in good correlation with the results reported in the literature for Whatman paper. For copier paper, the production of carbonyl groups at the increased absorbed dose is slower. As with the concentration of free trapped radicals (the central RES signal of irradiated cellulose), neither the concentration of carbonyl groups shows a saturation in the range (0-100) kGy.

A general conclusion of the study on the assessment of degradation induced by ionizing radiation in paper is that, for the low absorbed dose range (up to 10 kGy), the modification of the macroscopic properties of paper is predominantly governed by changes in the structure of the hydrogen bonds of the fibril material, and to a lesser extent by the cellulose degree of polymerization. That is why we have deepened the study with a series of considerations regarding the effect of low dose irradiation of radiation on the supramolecular structure of cellulose fibers.

In the study of the hydrogen bonding of paper pulp by thermogravimetry and differential scanning calorimetry applied to pure cellulose paper (Whatman), we have obtained new results on the possibility of using thermal analysis to characterize the structure of hydrogen bonds in the fibril material and confirmation of the assumptions regarding the strengthening of the structure of hydrogen bonds at low doses of irradiation. Hydrogen bonds are the basis of the supramolecular structure of cellulose and the three-dimensional fiber web, and also contribute to the thermal stability of the cellulose material. In the paper industry, the effects of formation and loss of hydrogen bonding to the mechanical properties of the paper, when water is absorbed or eliminated, are well known. The simultaneous thermal analysis in an inert atmosphere of nitrogen, carried out on samples from which the free water content has been eliminated, allowed the identification of a DSC peak with no correspondence in the mass loss, which we attributed to the decomposition of hydrogen bonds. Dependence on the absorbed dose of the parameters of this endothermic peak highlighted the preservation or even strengthening of the hydrogen bonding structure of the macromolecular assembly, at low doses of radiation (up to 10 kGy). By breaking the cellulose macromolecule, a change in the hydrogen bonds existing in the cellulose material is expected: formation of new extra- and intramolecular hydrogen bonds and/or strengthening of existing ones (decrease of the interatomic distance), leading, by crosslinking, to a global strengthening of the three-dimensional structure of intermolecular hydrogen bonds. When increasing the absorbed dose while reducing the degree of polymerization due to cleavage of beta-glycosidic bonds, the stronger hydrogen bonding structure may cause additional ruptures of the structural units of the macroscopic fiber (microfibrils and fibrils). As a result, the paper irradiated at relatively low doses shows a structure in which even if cellulose macromolecules exhibit a lower degree of polymerization but the hydrogen bonding structure is similar or improved to that of non-irradiated fibers. This fact also explains the results obtained in testing the mechanical properties of irradiated paper in the relatively small dose range of interest for radiation treatment in order to preserve the cultural heritage.

By studying the hydrogen bonding of paper cellulose by FT-IR spectroscopy, we obtained a confirmation of the proposed interaction mechanism for low dose irradiation. There is no clear and common understanding in the literature on the attribution of bands in the region (3700-3000) cm\(^{-1}\) (OH stretch). The attempts to describe this region include the deconvolution of 3-4 bands that are not directly identifiable in the original data. The data obtained for the crystalline component of natural cellulose (α and/or β), correlated with cellulose crystallographic models and data obtained by numerical modeling, allow a generic allocation of the bands: (3230-3310) cm\(^{-1}\) for vibration of the intermolecular hydrogen O(6)H ⋯ O(3), (3340-3375) cm\(^{-1}\) for the intramolecular O(3)H ⋯ O(5), and (3410-3460) cm\(^{-1}\) for the intra-molecular O(2)H ⋯ O(6). To identify and highlight the contribution of the three types of hydrogen bonds separately, we applied a deconvolution technique on the (3700-3000) cm\(^{-1}\) range, corresponding to the OH vibration. The new results we have obtained show that:
• Deconvoluted peaks corresponding to inter- and intramolecular hydrogen bonds on Whatman paper are positioned at lower wave numbers (higher energy) than those of copier paper. This may be due to better quality (higher degree of polymerization and crystallinity index) of cellulose cotton than cellulose made from wood. The proportion of intermolecular bonds (the ratio between the intermolecular boundary area and the total area of the non-deconvolved peak) is higher for the two copier papers, which explains their better mechanical strength.

• For Whatman paper, at doses lower than 10kGy, there is observed a shift to smaller wavelengths of the hydrogen bonding peak, corresponding to higher binding energies, consistent with the observations of hydrogen bonding strength from the thermal analysis study. Dose dependencies for copier papers (similar for the two types of paper) indicate a shift first towards higher wave numbers (weakening of the hydrogen bonding structure) followed by a shift to smaller wave numbers, so that at the end of the dose range tested is the position of the peaks is similar to that of unirradiated samples.

In the considerations regarding the correlations between the thermal and mechanical properties of the irradiated paper, besides the correlations between the mechanical properties of the irradiated paper and the thermal analysis parameters for the doses higher than 25kGy, we also highlighted correlations for the low dose range. The uncertainty of measurement is better for thermal parameters, both because of the analytical method and the better uniformity of the samples used for thermal analysis (paper disks with a diameter of 5.5 mm) compared to the large samples for testing the mechanical properties (> 10 cm$^2$). A good correlation was obtained between the elongation at break and the activation energy determined in the kinetic study. The "mirror" profile of the dependence of activation energy on the absorbed dose against that of elongation at break is noted. Taking into account that the mechanical strength of the paper is mainly given by the hydrogen bonds that make up its three-dimensional assembly, it can be concluded that the hydrogen bonding structure also influences the thermal decomposition process of the paper pulp. Thus, a more rigid system (with higher mechanical strength) has a lower thermal decomposition activation energy.

The study of the dose rate influence on the irradiation effects on paper was performed by simultaneous thermal analysis and vibrational spectroscopy, for a dose rate range of practical interest, encountered in industrial gamma irradiators (similar studies are found in literature only for mechanical properties of paper or for the high dose range). For copier paper, the end temperature of the thermal decomposition peak exhibits a linearly decreasing aspect, corresponding to a continuous decrease in the degree of cellulosic polymerization. This continuous decrease does not occur also at the end temperature of thermal decomposition for Whatman paper. The delay in the end of the thermal decomposition can be attributed to the hydrogen bonding effect that we have highlighted for Whatman paper: the shift of the hydrogen bond decomposition peak to higher temperatures, more important to the samples irradiated at the dose rate of 0.1 kGy / h than those irradiated at a dose rate of 4.3 kGy / h. Apparently, the hydrogen bond crosslinking effect is stronger at the lower dose rate. All tested samples show an increase in the concentration of carbonyl groups when increasing the absorbed dose. However, there are no significant differences (within the limits of statistical deviations) between the results obtained for the three tested dose rates. The influence of the dose rate in the range (0.1 - 4.3) kGy is insignificant for all three types of paper tested, both in terms of thermal decomposition parameters as well as on the evolution of carbonyl groups and the effect on hydrogen bonds evaluated by spectroscopy vibrational FT-IR.

At the end of the experimental part of the thesis I presented some examples of ionizing radiation treatment experiments performed at the IRASM irradiator of IFIN-HH for conservation of paper documents. They illustrate the need for an effective treatment for large quantities of objects, taking into account the real situations in which paper collections may arrive.

The experimental studies in this thesis, the confirmation of the hypothesis regarding the role of hydrogen bonds in the irradiation stability of the macromolecular ensemble of cellulosic material and the characterization of changes in this structure of hydrogen bonds under the action of ionizing radiation are elements that contribute to providing answers on the applicability of ionizing radiation treatment in the field of cultural heritage. In addition to scientific interest, they respond to a social need related to preserving information and cultural heritage from previous generations.
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