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RADIATION PROCESSING FOR BIO-DETERIORATED ARCHIVED MATERIALS AND CONSOLIDATION OF POROUS ARTEFACTS

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Riassunto

Il presente lavoro illustra le applicazioni delle radiazioni ionizzanti (radiazioni gamma) nel campo dei Beni Culturali. Nonostante il molto lavoro svolto, occorre approfondire la valutazione dei vantaggi e dei limiti delle applicazioni delle tecnologie nucleare per queste applicazioni. Inoltre, e' indispensabile utilizzare ben definite condizioni di irraggiamento (in termini di dose e intensità di dose, condizioni atmosferiche, pre-trattamenti dell'oggetto) seguendo linee guida condivise a livello scientifico internazionale. A questo scopo, la valutazione di possibili modifiche chimico-fisiche talvolta irreversibili indotte dalla radiazione ionizzante nei materiali trattati, definiti "effetti collaterali, rappresentano un importante aspetto da investigare al fine di garantire la salvaguardia dell'oggetto trattato e l'affidabile diffusione della tecnologia proposta. Le attività svolte presso l'impianto gamma Calliope dell'ENEA sono focalizzate sulla Conservazione e Prevenzione, con particolare riferimento alla rimozione di agenti bio-deteriogeni nel materiale d'archivio, e sul Consolidamento e la Protezione, in riferimento alle tecniche di consolidamento mediante radio-polimerizzazione *in situ* di materiale ligneo o lapideo danneggiato. Per quanto riguarda gli aspetti di conservazione, le tecniche di irraggiamento possono sostituire il tradizionale uso di metodi tossici o cancerogeni, risolvendo problemi associati ad aspetti di salute ed ambientali. La tecnica consente inoltre di trattare in tempi brevi e con eccellente riproducibilità, grandi quantitativi di materiale deteriorato, utilizzando procedure standard di controllo. Per quanto concerne i problemi di consolidamento, molti agenti biologici ed atmosferici possono indurre gravi e spesso irreversibili effetti di degradazione su materiale poroso, ligneo o lapideo. In questi casi, il consolidamento e la protezione superficiale avviene mediante l'impregnazione con sostanze naturali o sintetiche anche altamente tossiche, ma l'aspetto della penetrazione in profondità risulta comunque molto difficoltosa e spesso non garantita. Il trattamento del manufatto artistico con una soluzione diluita di precursori innovativi seguita da radio-polimerizzazione *in situ*, può rappresentare una valida soluzione sia dal punto di vista tecnico che ambientale per il consolidamento in profondità di materiale poroso.

Parole chiave: Beni culturali, Deterioramento, Consolidamento, Bonifica materiale archivistico, radiazioni gamma.

Abstract

This paper regards the application of ionizing radiation (gamma rays) in Cultural Heritage. Despite much work has been done, it is necessary to increase knowledge on the advantages and limitations of nuclear technology for this kind of application. Besides, the statement of well defined irradiation condition (in term of irradiation dose and dose rate, environmental atmosphere, pre-treatment of the cultural heritage object) and the proposal of shared guidelines is extremely desirable. From this viewpoint, the evaluation of the often irreversible physical-chemical modification induced by ionizing radiation on treated materials, namely "side-effects", represent an important goal to guarantee the safeguard of the treated artefacts and the a reliable diffusion of this technology. The ENEA activities performed at Calliope plant were focused on two different aspects: i) Conservation and preservation: bio-deteriogen eradication in archived materials, and ii) Consolidation and protection: degraded wooden and stone porous artefacts consolidation. As regards the conservation aspect, the radiation technology can replace the traditionally used toxic or carcinogenic methods, eliminating the associated health problems and environmental pollution. Large amount of bio-deteriorated objects can be treated in a very short time with excellent reliability, using controlled and standard procedures. Concerning the consolidation problem, many different atmospheric and biological agents, induce severe and somewhat irreversible degradation phenomena on wooden or stone artefacts (i.e. porous materials). Consolidation and surface protection of these degraded objects is usually obtained by the application of natural or synthetic consolidating agents but the penetration inside the porous material it rather difficult limiting the effectiveness of the treatment. Impregnation of the cultural artefact with a diluted solution of new formulation of consolidant precursors followed by radiation induced in situ polymerization represents a very promising solution to achieve actual bulk strengthening.

Keywords: *Cultural heritage, Deterioration, Consolidation, Archived materials recovery, Gamma radiation.*

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1. INTRODUCTION

Nowadays, ionizing radiations are being employed in a wide number of applications of great importance for both the scientific and industrial communities. Radiation processing are used in many sectors such as sterilization, polymer cross-linking (tapes, tubes, cables,), food hygienization, tyre belt vulcanization, etc. In the context of the peaceful use of nuclear and radiation technologies, IAEA promotes nuclear techniques, with special emphasis on gamma radiation treatment, for the characterization and preservation of Cultural Heritage artefacts including insects eradication, microorganisms disinfection and consolidation of degraded materials with radiation-curing resins [1]. Safeguarding the world cultural heritage is an important task for the whole community since evidences of the past have to be maintained in the present and restored for the benefits of future generations.

As cultural heritage objects are frequently unique and non-replaceable, scientific researches devoted to the application of different technologies for the characterization and preservation of cultural heritage are worldwide of great interest [2]. In the last decades, it was demonstrated that nuclear techniques are exceptionally suitable not only for non-destructive characterization of cultural heritage artefacts, but also in support of their conservation and restoration, as well as for their preservation through the use of radiation treatment.

The physical properties of electromagnetic radiation (i.e. gamma rays from ^{60}Co source) allow them to penetrate materials with extremely harmful effect on living organisms. By the irreversible denaturation or cleavage of nucleic acids, organisms and microorganisms, present on the surface and in the bulk of the irradiated objects, are simultaneously and indiscriminately devitalized.

The attack of microorganisms and/or insects, the so-called “bio-deteriorating agents”, can indeed cause a rapid, disastrous and often irreversible damages to cultural materials containing cellulose, starchy material, albumen, glue, vegetable proteins, dyestuffs, pigments, dispersing agents, and other additives that provide food sources for the infesting organisms.

The importance of bio-deterioration is underlined by the high frequency of the most harmful natural calamities occurrence (i.e. floods, earthquakes) that can affect books and archives, infecting and damageing a great amount of them. Moreover, bio-deteriogens can cause severe health problems for restaurateurs, archivists or librarians.

Consolidation and surface protection of degraded wooden or stone artefacts (i.e. porous materials) represent one of the most interesting challenge in the cultural heritage [3]. As known, many different atmospheric and biological agents, such as humidity, temperature leaps, biological growth or chemical attack [4-7], induce severe and somewhat irreversible degradation phenomena on these kind of materials.

Regarding stone artefacts and architectural structures, the main degradation effect consists in a sensible loss of their mechanical properties, increasing their fragility by mortar pulverization or causing great modification of surface aesthetical features. On the other side, ancient wooden cultural objects undergone many different chemical and physical changes, due to the biodegradable nature of the material itself. In this perspective, the use of high-penetrating ionizing radiation such as gamma rays is extremely suitable to induce the *in situ* polymerization of synthetic consolidating agents.

By gamma radiation it is possible:

- removing bio-deteriorating agents
- stopping the ongoing destructive process
- restoring the object of cultural value.

Other important advantages that can be mentioned are:

- physical method due to which no toxic or radioactive residues remain in treated item or environment
- due to the high penetration power of gamma radiation, large amount of bio-deteriorated objects can be treated quickly (probably the only method in case of emergency).

Despite much work has been done, it is necessary to increase knowledge on the advantages and limitations of nuclear technology for cultural heritage application. Besides, the statement of well defined irradiation condition (in term of irradiation dose and dose rate, environmental atmosphere, pre-treatment of the cultural heritage object) and the proposal of shared guidelines is extremely desirable.

The evaluation of the often irreversible physical-chemical modifications induced by ionizing radiation on treated materials, namely “side-effects”, represent an important goal to guarantee the safeguard of the treated artefacts.

One of the main obstacle to the diffusion of nuclear technology is effectively the negative effect that ionizing radiation such as gamma rays can induces in the polymeric materials (i.e.

paper, wood, resins) [8-11]. This effect consists in the de-polymerisation of the polymeric network, proportional to the absorbed radiation [12]. It occurs either directly on the macromolecule intermolecular bonds either indirectly through a chemical effect mediated by free radicals that could cause post-irradiation changes. The direct effect causes simultaneously a three-dimensional cross-linking and the breaking of the chains (i.e. bond β-glycosidic cleavage on cellulose, basic constituent of paper and wooden artefacts), measurable as a decrease of polymerization degree (DP) always proportional to the absorbed radiation dose [13-15]. Although both these processes occur at the same time, reticulation is prevailing at low absorbed doses while degradation (i.e. bonds rupture) becomes significant with the increase of the irradiation dose [16]. Finally, while cross-linking improves the mechanical properties of materials, the chains breaking acts on the contrary, with dominant effect over around 10 kGy [17].

Free radicals, very unstable and energetic short-life species (10^{-3} seconds), are responsible of post-irradiation effects also in the long term period since they can be trapped in the electrostatic cages of material structure. Throughout the indirect action of radiation induced free radicals, a key role is played by the oxygen present in the air during irradiation due to the oxidative degradation phenomenon [12]. The presence of this gas allows the formation of oxygen-containing very energetic radicals (such as peroxides, hydro-peroxides, superoxides, etc.) that easily react with the surrounding molecules. In this way, radicalic reaction are induced with a consequent and often macroscopic degradation of the material.

Since this process is related to the oxygen diffusion rate inside the material, it is clear that considering the same absorbed dose value, the longer the exposure time (low dose-rate), the greater the resulting damages [12, 18].

However, since the production of free radicals is proportional to the radiation dose, it is possible to minimize the oxygen degradation operating at dose rate as high as possible (but compatible with the treated material) or performing the irradiation tests in inert atmosphere or in vacuum [19, 20].

Considering the doses suggested for treatment of disinfestation, it was demonstrated that the radical degradation effects in these conditions are insignificant [1].

Side-effect evaluation can be carry out identifying one or several physical, chemical or structural parameters that can be directly measured after appropriate methodic procedures definition.

Many destructive or non-destructive techniques are employed to characterize the radiation damage on the treated materials. Some of them can be applied on different kind of cultural objects, such as polymeric-containing or porous materials: mechanical tests (tensile strength, tearing, folding and breaking resistance, micro-drilling to the surface hardness evaluation, flexural resistance, as example), optical measurements (diffuse blue reflectance factor, light absorption coefficient, light scattering coefficient opacity and brightness measurements), spectrophotometric analyses to evaluate the chromatic parameters of the materials surfaces (CIE L* a* b* space color) and thermal analyses (TGA, DSC, DTG) [21-24]. To achieve a more complete characterization of the objects, spectroscopic techniques such as XPS, XRF and AFM can be used for specific study of their surfaces (also in case of painting), while FTIR, X-ray diffraction, NMR (relaxometry and imageing) and ESR are suitable for the whole material characterization [25-29]. Very interesting information are obtained by TEM, SEM-EDX microscopic analyses or by X-ray tomography [30, 31]. Generally, it is of great interest to perform the materials characterization taking into account the water absorption properties. In this sense, evaluation of water uptake by capillarity and hydrophobicity could be carried out by ultrasonic velocity tests, gravimetric and contact angle measurements [32]. Moreover, pore size distribution and mercury intrusion porosimetric analyses, even if destructive tests, are very often performed on cultural objects. Finally, chemical properties of cellulose-based materials (pH, Kappa Number) and of stone (ionic composition modification) can be analytically defined while ion chromatography and GC/MAS could be applied to identify the chemical species produced by degradation processes [33]. Additional techniques are of common use for the investigation of polymeric materials (i.e. cellulose and consolidating agents). Among them, viscosity measurements and size exclusion chromatography (SEC) are suitable to evaluate the polymerization degree (DP) and the macromolecules sizes while DOSY-NMR technique give information about the dimensions of the monomers and co-polymers, with direct outcome on their diffusion properties [34-37]. Several of the above described tests are regulated by international standard procedures (ISO, EN, ASTM, etc.)

Finally, it is demonstrated that is extremely useful to perform accelerated ageing tests to investigate the combined effect of irradiation and of other parameters (such as humidity, thermal cycles, aggressive atmosphere) simulating the drastic environmental conditions to which the artefacts are subjected during particular natural calamities.

The aim of our activities will be focused on the irradiation procedure definition for:

a) conservation and preservation: mass treatment of deteriorated books and documents, stored in libraries and archives, for their recovery from the most important bio-deteriorating agents;
b) consolidation and protection: porous cultural artefacts treatment by ionizing radiation *in situ* polymerization of resin compounds.

Material characterizations will be carried out to determine the effect of ionizing radiation on the cultural objects, using different irradiation parameters and procedures.

1.A CONSERVATION AND PRESERVATION

Archives and libraries disinfection/disinfstation

For years, new methods have been sought for the recovery of materials suffering from various forms of bio-deterioration and many requirements have to be fulfilled by these technologies: effectiveness against all infesting organisms, high efficacy degree, harmless for operators and environmental safe, absence of side-effects beyond those considered acceptable and inevitably in almost any treatment process, but above all no alteration of the intrinsic feature characteristics of the treated material.

Up today, decontamination of bio-deteriorated material is usually performed with ETO but this fumigation treatment, owing to the last results of more in-depth research about its harmful effects either for human health [38], environment as well as in some case even for cultural heritage itself [39-49], has been banned in many Countries and probably its use will no longer be allowed in the future for such purposes. In particular it has been established that despite repeated changes of air performed on fumigated materials it is impossible to remove completely the volatilized residues of ETO. Studies comparing the relative capacity of different materials to off-gas residual ethylene, demonstrated that photographic film (plastic materials in general) show a level of release slower than other supports [50, 51], remaining harmful to those who handle them. Likewise it was also noted that residues remain on new card printing, wood fragments, cardboard and leather [52].

Alternative methods instead of chemical substances, are presently being investigated and evaluated such as ionizing radiations that have the advantage of a higher penetrating power allowing to treat considerable amounts of damaged materials in a reasonable short times leaving restored objects free from contaminants.

The international scientific community shows a clear convergence of interest about the need for studies both to evaluate the effects of ionizing radiation on the physical-chemical properties of the irradiated objects and to identify the dose required for cleaning treatment, considering that the main obstacle to the use of radiation is the decrease of the degree of polymerization of the cellulose.

The effectiveness of ionizing radiation on bio-deteriogen organisms has been further confirmed [53, 54] as well as the need to further study on the radio-induced effects [55, 56]. On the basis of physical and microbiological obtained results, a dose of treatment ranging from 5 to 7kGy has been recommended to obtain a significant reduction of the microbial load with minimum negative effect on the paper substrate [57].

Regarding to the real applications of these technologies, one of the first reports on the irradiation of a large amount of paper documents has been the collection Gantt belonging to Johns Hopkins Hospital in Baltimore - USA (manuscripts, photographs and medical records dating from the early twentieth century), strongly bio-deteriorated. All the material was treated with doses of 4.5kGy (only colorimetric and biological tests were carried out at the time, 1980); twenty years after the treatment visible adverse effects were still not highlighted [40].

Another intervention by gamma irradiation was performed to remediate the university library Morgan Library in Fort Collins, Colorado (USA) following the flood of 28 July 1997. Thousands of bio-deteriorated books, periodicals and newspapers were irradiated at doses of 15kGy and, without performing post-irradiation analysis, materials were relocated in the rooms cleaned up from the mud [58].

In Romania since 2001 a plant operates at the IRASM - Department of National Institute for Physics and Nuclear Engineering and in recent years wooden objects (iconostasis and icons), paintings and furniture have been irradiated as well as books and films [59-61].

On this last category of cultural heritage, doses ranging between 25 and 50kGy did not change their mechanical properties [62]. On the contrary, different conclusions had been achieved

with the same type of film probably due to the different methods applied to evaluate the synergistic effect of artificial ageing and irradiation treatment [63].

Even in the UK successfully trials were carried out on archaeological wood; studies have shown the absence of side-effects even when material was subjected to doses higher than those required for sterilization treatment (20-30kGy) [64].

In Holland at TNO (The Netherlands Organization for Applied Scientific Research), doses < 10kGy are indicated as effective in restoring archival material from microscopic fungi [65], likewise in Germany about 15-20,000 volumes of the library of Leipzig have been successfully treated [66].

Moreover in the last 25 years, the plant placed at Ruber Boscovic Institute of Zagreb (Croatia) has treated about 5,000 sculptures in painted wood, parts of altars, furniture, musical instruments, paper materials and leather. The treatment carried out at low doses (1-2kGy) was applied as "quarantine measure" before the objects exposition in the Museum of Modern Art [67].

In the Czech Republic, at the Museum Central Bohemian Roztoky Prague, it has successfully tested the radiation of about 1800 objects in textile, paper, ceramic and wood, of various sizes [68].

Experimental research on the potential of gamma radiation for the recovery of archives and libraries dated back as far the 1960, when in the context of the conservation of goods of cultural value, the radio-resistance of the most significant microbial stocks were tested [69-71].

The recovery of different types of bio-deteriorated materials through gamma radiation has been studied and carried out all over the world and, even if the efficiency of ionizing radiation is confirmed, unfortunately there are different opinions about the correct radiation dose to be used for a real disinfection/disinfestation. Moreover, the radiation effects on the intrinsic properties of paper are not completely investigated.

The effectiveness of gamma radiation (16kGy) has been demonstrated able to inactivate several fungi isolated from naturally contaminated book but the dose effects on chemical-physical properties of damaged paper has not been verified [54].

The effects of gamma rays on bleached eucalyptus pulp prepared in laboratory were studied. The doses ranging from 3 to 15kGy showed no significant changes but results were gathered only from test methods for mechanical and appearance properties [55].

Three categories of papers were tested to establish the irradiation dose for paper decontamination: Whatman paper, contemporary copier type paper and papers from archives and collections 40-80 years old. Results allowed to conclude that a dose range of 5-7kGy ensures a significant decrease of microbial load with minimal negative effects even if only mechanical test and thermal analysis were carried out to verify possible side-effects [57].

In order to simulate a repeated irradiation over time, doses of 25kGy and 50 kGy were tested on paper and different tests were performed to study cellulose degradation: mechanical and colorimetric, EPR, thermogravimetric TGA-DTG and DSC (dynamic scanning calorimetry). Results showed the necessity to evaluate lower doses have (2-12kGy) specially in case of historic paper [60].

Scientific data on the possible negative effects on paper *substratum* reported in the literature, are often in contrast about mechanical modification at doses up to 10kGy [70, 72, 73].

The use of low radiation doses (≤ 4kGy), which ensure disinfestation treatment and good reduction of the microbial load, if combined with a thermo-hygrometric control of conservation premises, allows to set its efficacy with doses lower than those required for sterilization, since books and documents are kept and used in not sterilized conditions [74]. Thus the target will be the reduction below the dangerous threshold of bio-deteriogenous organisms applying more controlled doses [75].

Accelerated and artificial ageing is considered an effective tool to evaluate the changes induced by other treatments and to verify the irradiation effects over time. Scientific literature shows apparent contradictions. Our experience lead us to state that the ageing treatment (carried out according to ISO 5630/3 regulation: 80°C at 65% RH) does not cause any significant modification of the material in term of polimerization degree and mechanical and physical parameters [76]. A synergic effect on the polymerization degree was verified between thermal ageing at dry temperature of 105°C for 72 h and irradiation at doses greater than 8-10kGy [77]. UV radiation was used to artificially age five different types of paper previously irradiated at a dose of 14,4kGy. Gathered results showed that the damage of mechanical properties originated by accelerated photo-ageing was much larger than that induced by gamma rays. Moreover, irradiated and control samples experienced similar damage when subjected only to UV ageing [78].

In the case of irradiated films, the different results obtained are probably due to different temperatures combined with different humidity conditions or by different kind of radiation

(UV rays) [62,63]. Taking into account that the effects of synergic treatments are strictly dependent not only on the type, intensity and duration of the selected method but also on the sequentiality of the ageing, the paper artificial ageing carried out at 105°C for 72 h could be considered too dramatic if aimed at simulating a natural process [75].

1.B CONSOLIDATION AND PROTECTION

Porous materials consolidation and preservation

The main goal of consolidation treatments is the preservation and protection of original artefact, making them suitable for future exhibition or use. Usually, the consolidating agent, in liquid form, penetrates inside the porous material and, becoming solid, imparts an increase strength to the artefact [24]. Depending on the seriousness of the artworks deterioration, partial or complete impregnation with consolidants (usually polymeric compounds) could be necessary [79-82].

Several features influence the choice of the most suitable consolidant [80]. First of all, the consolidating solution must not damage the material itself: shrinkage or swelling during treatment, volume or surface deformation, use of too much stiff or easy to degrade agent might be absolutely avoided. Moreover, in case of employment of aqueous solution, it is necessary taking into account the increase of humidity inside the porous material and the consequent dimensional instability while synthetic resins, during the exothermal solidification process, produce an increase of temperature inside the cultural object that has to be minimized. Finally, long lasting consolidation effect together with negligible changes from the aesthetic point of view are required and the use of nontoxic solvent and a sort of reversible process are highly desirable [83-85]. However, although reversibility is one of the most important requirements for restoration activities, none of the methods or the products basically used for consolidation of porous materials present this property. That is the reason why, even though the appearance of the object remains undiminished, this practice is deliberately limited to those situations in which mechanical properties should be significantly strengthened and when the preservation of the object has been significantly affected by degradation processes [83, 86].

To obtain a complete reinforcement of the porous artefact it is extremely important to evaluate its porosity characteristics and the properties of the consolidating agent [87]. This process involves two phases, the first being the partial or total impregnation of the cultural object with consolidant solution and the second its curing.

The penetration depth of the consolidant depends on the material permeability to liquids, on the impregnation methods and on physical-chemical properties of the specific consolidant solution (i.e. viscosity, molecular weight, concentration). In particular, since the porosity of the cultural objects increases with the degradation degree, it is necessary to find a compromise between the type of consolidant and the solvent to ensure the most homogeneous and less invasive consolidant solution penetration into the damaged artefact [88, 89]. Regarding the solvents, the most desirables are those that not only show low viscosity (easy to penetrate deeply into the object) and medium volatility (removable also from the material bulk) but are also not harmful and environmental friendly [90, 91]. Moreover, a not correct choice of the solvent for solubilizing consolidating products can adversely affect the operation or even damage the work of art, especially if painted.

In the practical use, the impregnation of the consolidant is carried out in many different ways. A common method traditionally employed consists in the deposition of the consolidant solution on the artefact surface by brushing or spraying: the penetration is obtained by the repetition of the process for several times. All the operation are carried out at room temperature but the effectiveness of the treatment is not ensured, since the dimension of the consolidant often prevents its diffusion into the whole artefact volume, limiting the consolidation to its surface [92]. On the other hand, better results are obtained on dried porous objects performing the impregnation under vacuum or pressure application.

Once completed the impregnation phase, the curing process, responsible for the consolidant fastening within the porous structure, is achieved by means of chemical or physical methods. The first ones are the most applied and the solidification of the consolidating agents is usually obtained in presence of suitable catalysts or radical iniziators (i.e. AIBN 2,2'-azoisobutyronitrile, etc) activated by thermal treatment or light sources [93, 94]. In the physical methods, ionizing radiations, such as electrons or gamma rays, supply themselves the energy required for the consolidation without any additional processing or reagents [95, 96]. Radiation induced polymerization indeed is a widespread and well accepted technology used for industrial applications [97]. This process can be carried out in bulk, in solution, in

emulsion (suspension), in the gas, solid and in the glassy state, just as in other initiation methods (chemical, thermal, photochemical initiation, etc.). Penetrating radiation, in particular gamma radiation, ensures regular initiation throughout the bulk of the solid monomer [1]. Radical chain polymerization, involving very reactive intermediates, occurs in three steps. The first stage of the reaction is the initiation, in which free radicals (typically peroxides) are created directly by the ionizing radiation [98]. In the propagation step, the free radical is propagated down the polymer chain leading to the formation of active oligomers. During this step, the polymeric precursor undergoes to cross-linking and the formation of gel accompanied by heat production (gel effect), is evident. The final step, in which two molecules containing free radicals react and form the final product, is called termination. A significant advantage of the use of radiation is that the processes can be considered "solvent free" respect to conventional synthesis procedures thereby reducing or avoiding the presence of additives that could be potentially harmful and of the purification and controlling of the final reaction products [1, 99, 100]. Furthermore, the reaction rates can be precisely controlled during any required period of time by modifying the irradiation parameters (dose, dose rate).

Wood and stone consolidants are usually solids dispersed in aqueous or organic solvent and can be divided into natural and synthetic substances. The properties of natural, traditional consolidants such as proteinaceous glues, drying oils, waxes and natural resins are well known because of their long period of use. Nevertheless, the disadvantages of natural consolidants cannot be ignored, particularly the poor penetration, the low degree of strengthening, the sensitivity to changes in moisture content of the treated materials.

Synthetic consolidants for wood can be divided into thermoplastic resins, elastomers and thermosetting resins [101, 102]. Thermoplastic resins (i.e. acrylic- and vinylic-based polymers) soften when heated and become formable, but upon cooling become solid again: this process can be repeated several times. These polymers, namely the acrylic resins dissolved in organic solvents, such as Paraloid B72 (or Acryloid B72), are frequently used in porous objects conservation [103]. Although they are able to impregnate a thin outer thickness of materials, they can induce a substantial increase of mechanical strength [23]. Recent works demonstrate the inadequate stability of the acrylic resins after accelerated ageing [80, 104-107] and the difficult removal after long time from the artefact [108, 109]. Thermosetting resins (i.e. epoxy compounds), highly penetrant, are initially soft or liquid and become irreversibly hard and in some case brittle upon curing. Moreover, an excessive yellowing is

shown during time [110, 111]. Whereas thermoplastic resins, due to their molecular structure, are soluble in suitable solvents, thermosetting resins form a three-dimensional network and cannot be dissolved. Since the solubility of a given resins determines its reversibility, thermoplastic resins should be preferred to thermosetting ones in conservation. Elastomers (i.e. unsatured or vinylic bond presence) consist of scattered cross-linked chains. At room temperature and above, they are of rubbery consistency, do not melt, present limited solubility and usually serve for consolidation by use as gap fillers [112].

Many other wooden consolidants are investigated: polyethylene glycol (PEG), soluble in water, is suggested for waterlogged application, despite this material degrades over time; aldehydic resins present a good stability and high plasticizing ability; crystalline cellulose, resistant to acid attack and not hygroscopic as the amorphous form [113]. Fluorous polymers, even though harmful, are sometimes employed to improve the humidity protection [96].

Considering the stone artefacts, apart from acrylic and epoxy resins, inorganic consolidants are proposed in different form (liquid solution, suspension, colloids, nanoparticles-containing emulsions), with the presence of calcium or barium hydroxide [114, 115], ammonium oxalate, silica [23] or other compounds [116-118]. Alkoxysilane-based polymers (i.e. TEOS), in general used in form of oligomers, are the most applied mainly due to their high penetration ability and for the negligible impact on the permeability properties of the consolidated stones [23].

Therefore, the effectiveness of a good consolidation process by the application of a specific polymer depends essentially on the amount on solid consolidant remaining into the object (consolidant retention), on the penetration depth and on the uniformity of distribution.

The main problem of polymeric consolidants is related to their macromolecular nature. Due to their molecular sizes, the penetration inside the porous material it rather difficult and hence the impregnation depth is often very small, the polymer being confined to the superficial layers: in this case only protection but not consolidation is achieved [119].

To overcome these problems, an impregnation of the cultural artefact with a diluted solution of consolidant precursors (i.e. monomers or oligomers) followed by an *in situ* polymerization is strongly suggested. The low sizes of these pre-polymeric species allow a more deep diffusion inside the porous materials and a consequent bulk strengthening.

The polymerization of monomers, oligomers and pre-polymers can be initiated by chemical addictives such as catalists, initiators, hardeners or accelerators or by physical means such as

temperature, light or ionizing radiation, as above discussed. These methods can also be used in combination, e.g. in thermo-catalytic processes. Curing by chemical reactions is of great importance for wood consolidation because it can be performed at room or at high temperature. In the last case, since the material could undergone damages during the consolidation process, the choice of the consolidating agent and the suitable addictives is essential. For example, while epoxy resins require the presence of a hardener for the room temperature curing, acrylate and unsaturated polyester resins polymerization is possible only with an accelerator and a temperature increase, necessary for the catalyst activation. Thermo-catalytic polymerization, using different starting monomers, is widely applied for the production of wooden composite materials for engineering applications. A mixture of methyl methacrylate and styrene monomers (1:1 molar ratio) which is under vacuum and pressure impregnated into the cellular structure of a fast-growing poplar wood was tested [92, 120]. Wood-polymer composites was produced by using combinations of methyl methacrylate, 2-hydroxylethy methacrylate and ethylene glycol di-methacrylate onto sugar maple wooden samples, performing the polymerization and curing at different temperatures [121]. By this effective temperature-step process, a complete polymerization of impregnated samples is demonstrated, finding application also with styrene-glycidyl methacrylate [122] and furfuryl alcohol [123]. Thin film of MMA-EMA co-polymer was produced by low pressure non equilibrium plasma for the protection of papery material. The co-polymer, characterized also after accelerating ageing, showed very good behavior [124].

Furthermore, the possibility to produce via chemical process (with AIBN as initiator) different acylic co-polymers to be applied as protection for paper and textile materials was also investigated [94]. Depending on the monomer combination (i.e. EMA/MA, MMA/EA, MMA/BA), the temperature required for the process could be different and in some case not compatible with the material to be treated. The addiction of fluorinate compound in small amount improves the protective properties of the polymer.

In situ polymerization of a co-polymer ethyl methacrylate, methacrylate using AIBN initiator and heat [125-127] was carried out onto calcareous sedimentary stone samples. To increase polymer cross-linking and consolidating properties, the acrylic co-polymer were mixed with some plasticizers. The *in situ* polymerization is carried out both in bulk and in acetone solution with different percentages of solvent and initiator. The experimental procedure consisted of three steps: 1) capillarity absorption of the consolidating mixture; 2)

polymerization carried out at 50°C for 24 h and 3) purification of traces of solvent in a vacuum oven at 55°C for two days. The product obtained by the chemical *in situ* co-polymerization (using EMA/MA as precursors) was compared with the commercial product Paraloid B72 for application in stone artefacts consolidation [127].

In general, room temperature curing is to be preferred for cultural property because, especially in the case of polychrome objects or wood, the application of heat can cause irreversible changes due to simulate accelerated ageing. Moreover, using consolidants such as methacrylates, their vapor pressure raises so much due to the elevated temperature that, in spite of wrapping, large quantities of consolidant escape from the impregnated object [79].

In this sense, ionizing radiation represents a really appropriate methods to obtain monomers polymerization without modification from the chemical (no addictives) and physical (no temperature increase) point of view. Furthermore, the high penetration power of gamma rays allows a bulk polymerization with a production of very homogeneous product.

Many wood and stone consolidation activities were carried out worldwide since the sixties, obtaining very good results [1, 95, 67, 129-130]. During the late seventies, the consolidation of many degraded wooden artefacts was carried out by using more appropriated radiation-curing resin based on unsaturated polyester and styrene [61, 131, 132]. This latter was also implemented in conservation of waterlogged archaeological artefacts as an alternative to conventional treatments with water-soluble polymers (PEG). Irradiation and redox polymerization of methyl-methacrylate and butyl-methacrylate homo-polymers and co-polymers onto undamaged and damaged wood samples, was compared obtaining a higher yield of polymer in the wood using gamma rays [133]. Radiation induced co-polymerization of acrylonitrile, allyl glycidyl ether and allyl alcohol, with appreciable improvements of mechanical properties and decreasing of water uptake in wood samples was also investigated [134-136]. *In situ* X-ray iniziated polymerization of wood blocks impregnants based on hydroxyl ethyl methacrylate (HEMA) monomers was performed [95]. The dose rate effect was investigated, demonstrating that lower values enhances the propagation step in the monomer polymerization. A total polymerization was obtained al doses <25kGy, well acceptable for wooden substrates. The presence of hydroxyl functional group enables the polymer to enter into the wood pores with the creation of stable hydrogen bonds with the cellulose itself, giving a good consolidating results.

Finally, studied the MMA gamma induced polymerization by the reversible addition-fragmentation chain–transfer (RAFT) method was investigated [137]. In this case, the process was conducted at room temperature and without the use of any thermal or photo-initiator, being the gamma radiation itself the initiator source. The dose rate effects was also investigated [138] in the gamma radiation induced polymerization of MMA and BA micro-emulsions: the higher the dose rate value, the lower the polymeric particles sizes. Depending on the starting monomer, the absorbed doses were in the range 4-20kGy.

Finally, a very important aspect regarding polymeric materials is the possibility to characterize their stability during time by accelerated ageing. The main factors causing age-related degradation of polymer are: temperature, radiation dose rate and total dose, oxygen, moisture, mechanical stress, ozone and contaminating chemicals [139].

It should be emphasized that real employment conditions usually involve synergic effects between two or more of these factors. In particular, ozone effects are only likely to be significant in polymers containing high proportions of double bonds in the molecular chain. Moisture is another potential ageing parameter that has not been adequately studied in its effects on degradation. For many of the polymers, oxidation is the dominant ageing mechanism and is initiated both thermally and by irradiation. In PVC, as example, which was widely used, both of these mechanisms can result in embrittlement of the materials.

The most commonly used accelerated ageing tests apply higher temperatures and dose rates than are normally experienced by the material. Furthermore, could be desirable perform simultaneous radiation and thermal ageing in these accelerated tests [140, 141]. Therefore, in many cases, such tests are carried out by using sequential ageing, either thermal followed by radiation, or vice versa [142]. In this sense, it was for example demonstrated that the mechanical degradation of ethylene-propylene co-polymers is more severe if thermal ageing followed gamma irradiation, while in the opposite case the degradation is practically similar to that due to only irradiation [143].

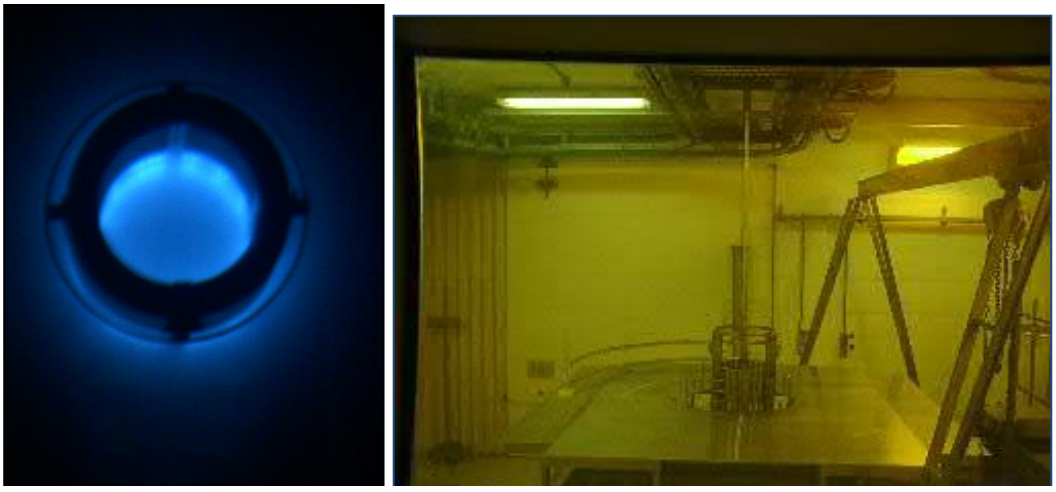
2. ENEA ACTIVITIES – Calliope gamma irradiation facility

The Calliope gamma irradiation facility (ENEA Casaccia R.C., Rome, Italy) in the last decades has been deeply involved in research and industrial activities such as agricultural, radiation processing on industrial materials (polymers and optical fibres) and on devices to be

used in hostile radiation environment (nuclear plants, aerospace experiments and High Energy Physics experiments), scintillating materials (crystals and glasses) as detectors in High Energy and Medium Energy Physics experiment, ionizing damage evaluation tests on electronic components [144].

Located at the Research Centre ENEA-Casaccia, the Calliope plant, was built in 1967-68 to carry out research activities in radiation processing research on industrial materials (polymers and optical fibres) and on devices to be used in hostile radiation environment such as nuclear plants, aerospace experiments and High Energy Physics experiments. The Calliope facility is a pool-type irradiation facility equipped with a ^{60}Co γ source in a high volume (7×6×3.9 m^3) shielded cell: the emitted radiation consists of two γ photons of 1.173 and 1.332MeV emitted in coincidence, with a mean photon's energy of 1.25MeV (Fig 1).

The maximum licensed activity for Calliope plant is 3.7×10^{15} Bq (100kCi) and it is possible to perform at the same time irradiation tests with different irradiation parameters (dose, dose rate) [145].

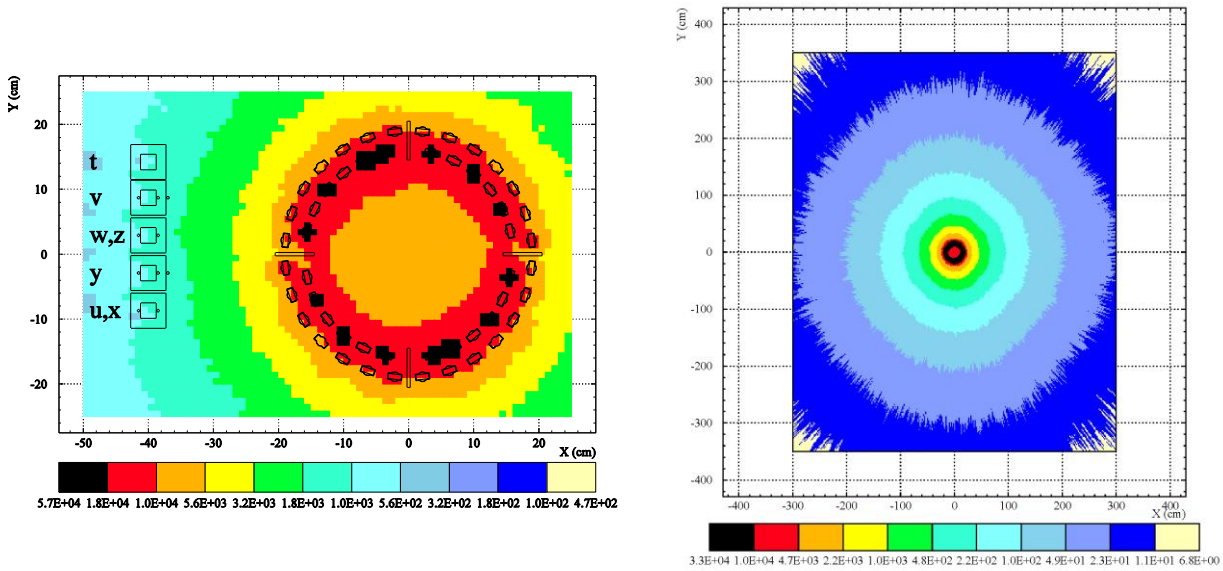


a) b)

Fig.1: Calliope irradiation Facility: a) Cherenkov effect b) Steel platform covering the pool, photographed through the yellow lead window of the Control Room

In radiation processing applications the measurement of dose during irradiation is of fundamental significance. The absorbed dose needs to be measured and its reliable measurement is used to document the successful execution of the irradiation tests, whether or not the required dose was delivered to the material within the given specification [146]. Due

to this reason, the Calliope facility is equipped with dosimetric laboratory, essential to obtain a precise measure of the absorbed doses in materials during irradiation. Different types of dosimeteric methods are used: Fricke absolute dosimetry (in the range of 20-400Gy), Red Perspex (in the range of 5-40kGy), thermoluminescent dosimetry (very low dose, < 20Gy)and EPR-alanine dosimeter (about 500kGy). Among them, the solid state dosimeter methods (Red Perspex and EPR-alanina) are relative measurement systems, periodically calibrated with an absolute dosimeter method, which is represented by Fricke dosimeter [145, 147]. A simulation of the dose profile inside the irradiation cell was performed by Fluka code (Fig.2).



a) b)

Fig.2: Top view x-y of the dose profile represented by color code (Gy/h) simulated by Fluka code: a) in region near the source; b) inside the irradiation cell. Data are referred to 2005.

The characterization of the irradiation effects on materials is performed at the Calliope laboratories. Transmittance and reflectance optical analyses in the UV-VIS-NIR range are performed by a double beam spectrophotometer (Perkin-Elmer Lambda 950) equipped with an integrating sphere, necessary in case of diffusive samples. Infrared spectra are recorded by FTIR spectrometer (Perkin-Elmer Spectrum 100). The same instrument is supplied with HATR sampling accessory for the Attenuated Total Reflection measurements and with gold integrating sphere for IR reflectance analyses. Both these instruments allow to perform measurements in inert gas atmosphere. Free radical species induced in the materials by gamma irradiation are detected and studied during time by an X-band Electron Spin Resonance spectrometer (Bruker *e-scan*). ESR spectra can be recorded in the temperature

range 77-298K and in different atmosphere (O_2, CO, N_2, Ar). A steady state fluorescence spectrometer (Edinburgh Instrument FS 5), characterized by excitation range of 200-1000nm and emission range of 230-870nm is used to investigate many different materials. In the laboratory are also present oven and furnace (T_{max} = 1200°C) to carry out thermal treatments or ageing cycles and a Dynamometer (Instron 6022) equipped with optical estensometer for mechanical tests on polymers. A high vacuum system is also available to perform tests in absence of oxygen. Viscosity measurements for the determination of the polymerization degree are carried out by a suitable viscometer.

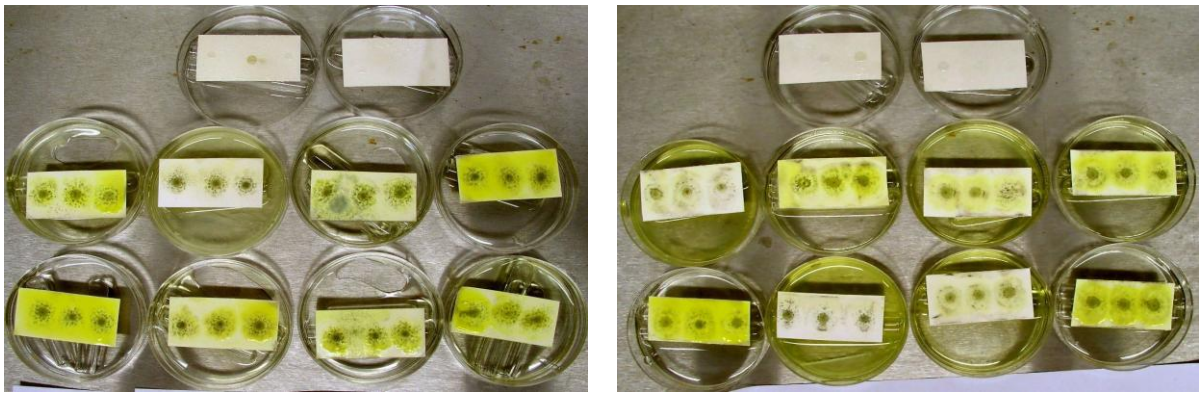
Microbiological laboratory instrumentation (autoclave, incubator, analytical balance) allows to investigate the post-irradiation effects on cellulose based materials. In particular, it is possible to: a) verify the gamma irradiation effects on microbiological load (bacteria and/or microfungi); b) assess the gamma treated paper vulnerability evaluating microorganisms development and erosion caused by chewing insects (*Blaptica Dubia*).

2.A ENEA Research on bio-deteriorated archieved materials

In particular in ENEA laboratories, gamma radiation has been examined from various points of view especially as concerns its efficacy and its effects, also associated with accelerated ageing to verify a radiation effect over time, on pure cellulose (gamma rays tested also combined with humidity, low temperature), permanent paper (radiation tested with associated treatment to study the influence of oxygen and the influence of water), and inks [76, 148, 149]. Moreover, further experimental trials were carried out to investigate whether, and up to what level, the chemical and physical changes induced in paper (newspaper, magazine, permanent paper and cellulose) by irradiation and/or ageing could negatively predispose this material, once treated, to the attack of destructive insects and microscopic fungi, increasing their harmfulness [150-152]. The results of all testing activities lead to the assessment that the ionizing radiation treatment is extremely efficient for the disinfestations against harmful insects and for disinfection against microfungi. Moreover using the necessary dose for an efficient treatment (0.2-0.5kGy for insects; 3-8kGy for microfungi), no significant harmful effect has occurred on the mechanical and physical properties of pure cellulose and of paper, on printing inks, on the vulnerability of treated material once subjected to infestation,

as well as infection due to bio-deteriorating agent. In addition results have demonstrated that damage caused by organisms is strictly related to the state of degradation of cellulose that is proportional to the absorbed dose; the microbial population decreases proportionally to the gamma rays dosage together with the de-polimerization of cellulose molecule. Even if the macromolecule of cellulose was depolymerised, this phenomenon was negligible at the recommended treatment dosage (3-5kGy) and in any case it did not alter the essential mechanical functional characteristics of the object.

With the same intent, studies have been extended to photographic material (developing out paper sensitized with gelatin-silver print. ILFORD-ILFOBROM 2.1 P) and results have put in evidence that no significant modifications both of the growth of microfungi and of the erosive action by chewing insects occur in the analyzed photographic paper irradiated with 3kGy, with respect to non irradiated paper of the same quality, as shown in Fig.2 and Fig.3 [153, 154].



a) b)

Fig.3: *P.chrysogenum* colonies developed paper samples: a) not irradiated; b) irradiated at 3kGy.

Moreover other experimental trials have been carried out to verify if gamma rays could change the fastness of different color dyes or pigment particles either they were suspended in the emulsion and they were added directly from photographer (Fig.4).

Results lead to conclude that the color fastness of treated photographic prints are not influenced by gamma radiation till 10kGy. Same data have been obtained with albumen, silver gelatin and collodion prints [155-157].

a) b)

Fig.4: Damages by of *Blaptica dubia* feeding on photographic paper samples: a) not irradiated; b) irradiated at 3kGy.

a) b)

Fig.5: Photographic paper, black and white, silver salts, turn sepia and coloured by hand dating from the 1920s: a) not irradiated; b) irradiated at 90kGy.

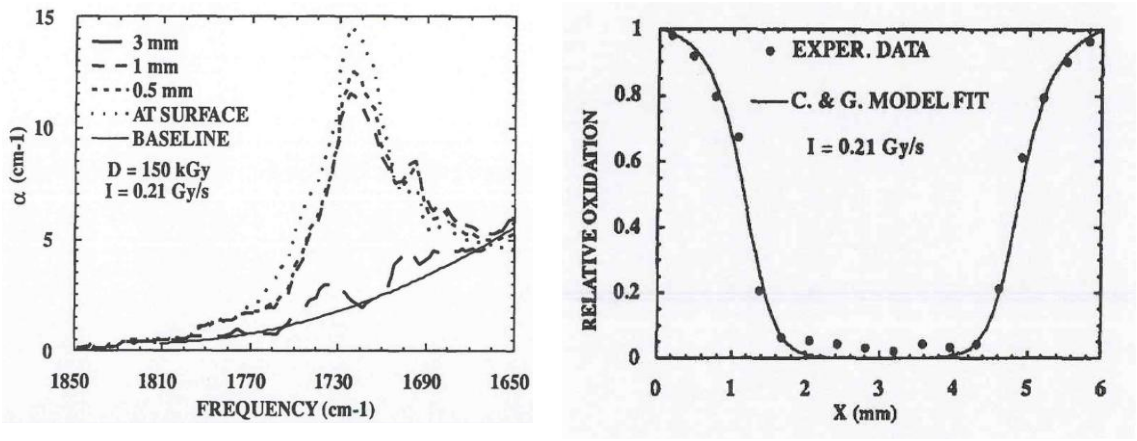
2.B ENEA Research on polymers under gamma irradiation

During the past decades, several activities regarding polymeric materials have been carried out in our Laboratory. In particular, the gamma irradiation effects on these systems

have been deeply investigated and the evaluation of the irradiation parameters (dose, dose rate) has extensively studied. Moreover, great attention has been posed on the definition of the optimal condition to minimize the undesired degradation side-processes.

Extensive studies were carried out on the ethylene-propylene co-polymer. In particular, great attention was paid on the degradation process of this system under gamma irradiation and on post-irradiation effects and accelerated ageing [143, 158-160]. ESR spectroscopy was demonstrated to be extremely suitable for the detection of free radical species induced by gamma rays: their identification and evolution after the end of irradiation was thoroughly investigated in the temperature range 77-333K. Some experimental results were shown in Fig.6 [161, 162]. The dependence of the oxidative degradation as a function of dose and dose rate was discussed and evaluated by FTIR spectra analyses [163]. Furthermore, the oxygen diffusion inside the polymer was measured by IR microscope obtaining an oxygen profile along the polymer thickness, as shown in Fig.6 [18].

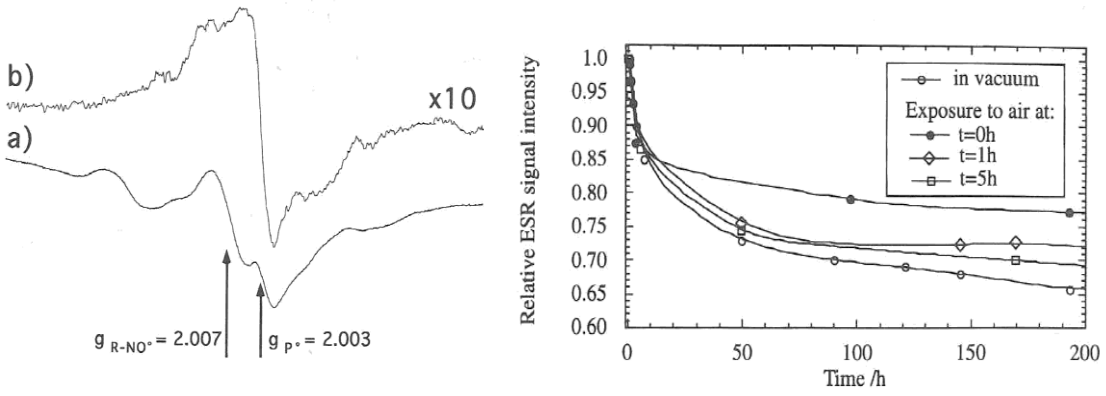
Finally, the analysis of the antioxidant added to the co-polymer was also performed by a specific characterization of the radical species [164, 165].



a) b)

Fig.6: a) Differential spectra of ethylene-propylene copolymer loaded with different amount of antioxidant sample D1 at four different depths; b) Oxidation profile for D! sample. The best fit parameters are a = 0 1100 and b = 0 20 [18].

The effect of gamma radiation on poly (vinyl chloride), mainly consistent in radicals production was investigated by EPR measurements at room temperature and the formation of conjugated double bonds was probed by UV–VIS absorbance measurements. Infrared measurements allowed to analyze the oxidation products [166, 167].



I) II)

Fig.7: Ethylene-propylene rubber samples: I) ESR spectra of samples measured soon after irradiation at 100 kGy (dose rate 0.3 Gy/s) in air (a) and in vacuum (b); II) relative ESR signal intensity vs storage time. The samples were irradiated in vacuum at 100 kGy (dose rate 0.3 Gy/s). The sample holders were broken and the samples exposed to air at different times. [165].

Poly-vinyl-pyrrolidone (PVP) hydrogel, produced by irradiation of its aqueous solution, has been successfully applied in biomedical treatments. Mechanical properties have been evaluated and correlated with the radiation dose [168].

The interaction between the carbon black reinforcement agent and a polymeric rubber matrix is investigated. Chemical activity of carbon black powder samples was enhanced using gamma radiation in the dose range 168–1000kGy and the radiation induced free radical concentration was investigated by EPR measurements. Activated powder samples were mixed with rubber and the bound rubber values of obtained compounds was measured by TG analysis. A comparison between EPR and bound rubber data shows that the greatest filler–polymer chemical interaction corresponds to the highest radiation induced free radical concentration [169].

Fluorophores poly-siloxane elastomeric scintillators, used for the detection of ionizing particles and neutrons, have been prepared with different composition and characterized by optical measurements and by excitation and fluorescence spectroscopy. The samples and commercial scintillators (EJ-212 and EJ-200) used as a standard underwent heavy irradiation with gamma-rays from a ^{60}Co source at different doses, up to 54kGy. The ex-situ light yield was collected immediately after the irradiation stage and after one month, in order to characterize the stability and the radiation hardness of scintillators produced with the different

blends [170]. Furthermore, many other commercial organic scintillators were characterized under gamma irradiation [171].

Interesting activities has been carried out focusing the attention on the chemical-physical properties of cellulose-based materials and on the modification induced by gamma irradiation. In paper structure, water plays a central role allowing the stabilization of the cellulose matrix and determining most of its mechanical properties. Using gamma irradiation to induce paper ageing, pure cellulose Whatman paper was characterized to get information about siting and dynamics of water rearrangement when cross-linking and degradation of cellulose occur. By NMR 2D technique a two-site (low- and high-mobility) residence model for water in the ultrastructure of cellulose was demonstrated. When cross-linking and degradation of cellulose occur due to gamma irradiation induced ageing, a significant fraction of water appears confined into low-mobility sites of the cellulose matrix. As the cellulose damage grows more pronounced, the two-site structure turns into a single-site water arrangement. In conclusion, using the NMR correlation maps, it is reasonably possible to obtain information to assess the damages in the structure of cellulose and its the ageing state [34].

Further investigation regarded the evaluation of gamma irradiation side effects on paper submitted to irradiation in the dose range 0-1000kGy, paying particular attention to the low absorbed doses (up to 10kGy), of great interest for cultural heritage applications. The structural modifications of cellulose, i.e. cross-linking and degradation processes, were studied by thermal analyses (TG-DTG) and FTIR spectroscopy and allowed a complete characterization of the cellulose-moisture interaction, as represented in Fig.8 [17].

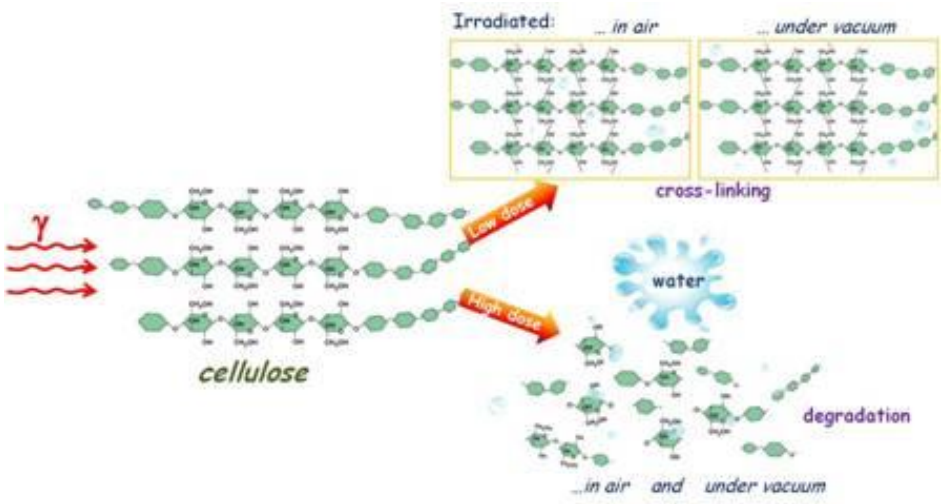


Fig.8: Representation of the moisture-cellulose interaction under gamma irradiation [17].

Ongoing activities is focused on the gamma irradiation *in situ* polymerization of methylacrylate and ethyl methacrylate monomeric solutions to obtain a co-polymer with similar characteristics of the most used consolidating products (e.g. Paraloyd B72) in cultural heritage. The optimization of the polymerization dose was carried out, verifying the same result at different dose rate values. Moreover, the investigation of the environmental condition was achieved performing the polymerization process in air and in inert atmosphere. Finally, further studies regarded the gamma induced MA and EMA homo-polymers preparation to investigate the effects of different parameters. The polymeric compounds were investigated by means of ATR-FTIR, ^{1}H and ^{13}C 1DNMR to achieve a complete characterization of the samples and of the effects of the different gamma absorbed dose on final product properties. DOSY-NMR technique gave information about the dimensions of the single monomers and co-polymer, with direct outcome on the diffusion into the degraded cultural object [172].
Finally, two-component epoxy resins and silicon compounds (resins and grease), used as optical coupling materials in high energy physics experiments, were tested under gamma and neutron irradiation. Their stability under irradiation at different absorbed doses and for long time after the end of irradiation was investigated in term of optical transmittance measurements [173].

3. CONCLUSIONS

Ionizing radiations are demonstrated to be extremely suitable for applications in cultural heritage, due to their effectiveness in bio-deteriogen eradication and in degraded porous materials consolidation. Radiation techniques have specific and indisputable advantages over classical procedures, such as no risk for the operators, no toxic residues and hence no risks for curators, visitors or the environment. Furthermore, large amount of deteriorated objects can be treated in a short time. However, to a large-scale and reliable employment of nuclear techniques for the conservation and consolidation of cultural heritage artefacts, an optimization and codification of irradiation procedures and of the methodologies applied to obtain a complete evaluation of the irradiation side- and post-effects are required. In this perspective, the creation of networking and international cooperation is essential to

share the knowledge on cultural heritage radiation treatment and to promote the proposal of extremely desirable guidelines and protocols.

In particular, this Project is focused on the irradiation procedure definition and on the irradiation side-and post-effects determination in conservation/preservation (archived materials) and consolidation/protection (new resins *in situ* polymerization on porous objects)

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