Gamma radiation-induced methods for the conservation and consolidation of cultural heritage objects – chromatographic, synthetic and chemometric approaches

The two main directions of this thesis are given by the use of high energy radiation for the conservation and consolidation of cultural heritage artifacts, being used as a disinfection method, respectively, as an initiator of the polymerization reactions.

Dyes identification from museum textiles provide significant information about their biological sources, geographical provenience or historical period. The main issue when it comes to the classical dye extraction using acid hydrolysis is the breakdown of glycosidic components into aglycons, leading to the loss of vital information regarding the biological source, therefore milder extraction methods with diminished hydrolysis processes, maintaining the glycosylated flavonoids intact are needed. This critical drawback is addressed by this thesis through the development of an alkanol-based supramolecular solvent (SUPRAS) used as a mild procedure, developed in order to preserve glycosides' information and the fiber itself. Aiming to evaluate the versatility of the extraction procedure, this approach was tested on protein fibers, dyed with flavonoids, anthraquinones and indigo dyes.

It is worth noting that while sterilization using high energy radiation is a widely used technique for the disinfection of cultural heritage objects, the literature has been deficient in detailing its effects on dyes. So far, research on this topic predominantly centers on the assessment of other historical object materials. This thesis has the potential to fill this gap by providing comprehensive insights into the impact of gamma irradiation on dyes. This is accomplished via a new analytical approach based on High Performance Liquid Chromatography with a Diode Array Detector hyphenated to a Mass Spectrometer, complemented by three chemometric methodologies applied for characterizing different dye classes, comparing extraction techniques, and assessing gamma irradiation treatment. The findings affirm that the newly proposed dye extraction method stands as a superior alternative, as it can reveal a more profound understanding of the original dye source compared to harsh acid-based extractions, while preserving glycoside linkages.

Emerging technologies based on polymeric materials are progressively developed in order to preserve and consolidate cultural heritage artifacts. Most of the macromolecular materials used so far exhibit issues related to toxicity and molecular oxygen inhibition. Consequently, this thesis aimed to obtain a chemically and dimensionally stable polymeric formulation, intending to use it as a consolidant of highly degraded wooden artifacts in order to mitigate oxygen inhibition from radical chain reactions, to increase chemical and thermal stability, as well as to obtain a stiffer consolidated artifact, therefore more resistant to deformation. The strategy was to achieve a covalently bonded 3D hybrid epoxy-acrylic polymer reliant on two types of thermosets that undergo irreversible crosslinking via ionizing radiation-induced polymerization, the polymer's structure and characteristics being tailored using specific dose rates, doses and monomers ratio. In addition, a novel thermal desorbtion-gas chromatography based approach was developed in order to assay the level of residual indoor borne styrene from museum artifacts consolidated through the classical radiopolymerization method using styrene-containing resins.

Various types of analytical techniques were performed in order to support the strategy and predictions regarding the synergistic effect given by gamma irradiation-driven crosslinking through simultaneous cationic and radical chain growth polymerization reaction mechanisms. It was achieved a homogenous polymeric formulation and wood-polymer composite materials with high modulus of elasticity, a good chemical resistance to various solvents and outstanding thermal resistance. Consequently, the consolidation methodology, as well as mechanical testing, analytical (HS-GC/MS, FTIR, STA, SANS) and morphological characterization (SEM, CT) of the resulted composites will be discussed.