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Original article

Epoxy monomers consolidant for lime plaster cured via a redox activated cationic polymerization

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ABSTRACT

Epoxy resins, widely used in conservation, still remain controversial materials. Considering some of the drawbacks that currently limit the application of epoxy consolidants, we present the application of the cationic ring opening polymerization as a novel method to cure the epoxy monomer in the restoration field. The cationic polymerization was carried out through a redox system based on the reduction of the iodonium salt in the presence of ascorbic acid catalyzed by a copper salt. The use of this initiator system for carrying out a suitable consolidant for lime plaster is considered. First, the film properties of the cured films were investigated. Then, the formulation was applied on a sample of plaster and its compatibility was verified. Its effectiveness as a consolidant product is explored through the evaluation of chromatic changes, mechanical strength, morphology of the re-aggregated material, and changes of the surface properties.

1. Research aims

The aim of the research is to take advantage of the good results obtained in the field of coatings through the cationic ring opening polymerization of the epoxy resins and export this technique to the conservation field. In fact, we consider that some of the benefits that this technique of curing has shown in other sectors can contribute to solving some drawbacks that currently limit the application of epoxy in the conservation of historical surfaces. In this study we show a possible application of cationic polymerization carried out through a redox system to create a non-toxic epoxy-based consolidant with a suitable pot-life, compatible with the substrate and that cures at room temperature.

2. Introduction

External plasters based on lime mortars often suffer some degradation phenomena such as detachment, lacunae and loss of cohesion. The ideal consolidant product should be able to restore the mechanical strength and other physical properties that the material had before the degradation. Moreover, it should easily penetrate the porous substrates and not remain on the surfaces to form a hard crust. It should not change the original color of the material. Finally, it should limit the penetration of moisture into the stone, allowing water vapor transmission [1]. In addition, economic, environmental and human safety issues must be considered in determining the compatibility of the treatment [2].

Epoxy resins have a wide range of applications thanks to their properties and versatility [3].

For deteriorated stone materials, and in general for outdoor exposed porous surfaces, consolidation with epoxy resin has shown to be an effective conservation process [4]. Durability, excellent adhesion properties, strength and high chemical and thermal resistance are the main features of these materials [4,5].

Some disadvantages have also been highlighted by operators and scientists during the recent decades. Until the seventies, the epoxides used were often those based on epichlorohydrin and bisphenol A, which possess some drawbacks such as a high viscosity and the tendency to degrade under UV radiations. The penetration depth depends on the nature of the treated stone, the composition and the viscosity of the consolidant system. In order to reduce viscosity, solvents are often used. Ideally, after its evaporation, the consolidant should penetrate deeply enough to reach deteriorated stone and remain as a thin layer that bonds the stone grains [6,7]. Despite this, the employment of solvents had shown some drawbacks. First of all, the solvent composition directly affects the reaction rate between the epoxy compound and the amine. When thermoplastic polymers are applied from solution, the nature of the solvent influences the conformation of the polymer in the solution and consequently the mechanical and physical properties of the final polymer film [8]. Moreover, when the solvent evaporates, uncured resin is deposited on the surface and after curing, it forms

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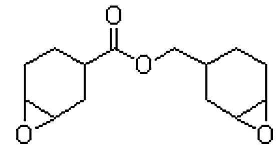
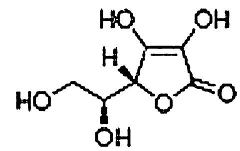
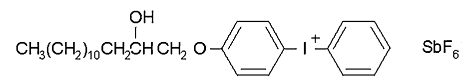
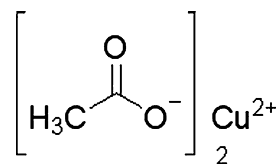
Table 1
Chemical structure of the organic materials.

Reagents	Structures
3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexyl carboxylate (CE)	
Ascorbic acid (Sigma-Aldrich)	
[4-[(2-hydroxytetradecyl)oxy] phenyl]phenyliodonium Hexafluoroantimoniate (Sigma-Aldrich)	
Copper acetate II (Sigma-Aldrich)	

a film which increases the refractive index of the surface making it more subject to photo-oxidative aging. Since the polymerization occurs only after solvent evaporation, it is difficult to avoid this kind of back-diffusion of the solution on the external surface. To minimise this, it is necessary to physically remove the stored polymer [9–12].

Cycloaliphatic epoxy resins have shown better characteristics than the epoxy based on epichlorohydrin and bisphenol A, in terms of their resistance to UV radiation and their impregnating capacity. Despite the good results obtained, as reported in several studies, some drawbacks are still present [13–16]. Firstly, the commercially available formulations contain a large amount of solvents such as isopropanol and toluene, which are toxic, in particular if the resin is applied on large surfaces in a closed environment. Secondly, it is known that amines used in the epoxy formulations as a curing agent, can be irritant to skin and eyes and cause problems to the operator.

An interesting alternative to the amine hardener is the cationic ring opening polymerization of epoxy monomers. The cationic process is gaining increasing importance in the fields of coatings and adhesives due to its peculiar characteristics and advantages, such as low shrinkage, good mechanical properties and good adhesion properties on different kinds of surfaces. Moreover, the monomers employed are generally less toxic and less irritant [17].

In the cationic ring opening polymerization of the epoxy monomer, onium salts, ytterbium triflate and lanthanum triflate are commonly used to generate a strong acid upon photodecomposition or thermal input [18–20].

Use of the cationic process is uncommon in the field of conservation, even if it can solve some of the problems described above [21,22]. Nevertheless, some drawbacks limit their employment in a restoration site, in particular the need of UV radiation or thermal input to start the reaction. For this reason, the huge benefit of redox chemistry is that it allows the activation of cationic polymerization at room temperature without an external input like heat or light. In fact, diaryliodonium salts normally used as photoinitiator of cationic polymerization can be applied in a redox-induced cationic polymerization [23]. Indeed, this redox reaction is based on the reduction of dyariliodonium salts. Any organic and inorganic compound or polymer capable of lowering or reducing the charges of the heteroatom of the diaryliodonium salt are considered reducing agents. Therefore, in literature, benzoins, reducing sugars, tin (II) compounds and ascorbic acid, which is one of the most used, have been investigated as reducing agents. Reduction of onium salt by ascorbic acid is catalyzed by a noble metal complex, such as a copper salt [23–26]. In this system the reaction takes place spontaneously at room temperature [27].

In this article we illustrate the results related to the application of an epoxy monomer, used as a consolidant for lime plaster, cured with a cationic polymerization mechanism induced by a redox reaction. The final objective of this study is to create an epoxy-based consolidant with a suitable pot-life in view of its application on large surfaces, compatible with the substrate that cures at room temperature without the addition of amines and other products that could be considered toxic. In the first part of this study, data related to the curing process and to the film's properties are reported. Secondly, the formulations were applied on plaster surfaces to verify their consolidating effect. These preliminary evaluations were based on measuring chromatic parameters, water absorption properties, penetration depth and morphological changes of the treated surfaces.

3. Experimental

3.1. Materials

3.1.1. Chemical reagents

The biscycloaliphatic diepoxy resin 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexyl carboxylate (CE, purchased from Sigma-Aldrich) was used as curable resin. The ascorbic acid, the copper acetate (II) and the onium salt, [4-[(2-hydroxytetradecyl)oxy]phenyl]phenyliodonium hexafluoroantimoniate were purchased from Sigma-Aldrich too. The structure of the starting compounds is reported in Table 1.

The iodonium salt, the ascorbic acid and the copper acetate are insoluble in the monomer and, for this reason, were dissolved as reported in Table 2. The ethanol used to dissolve the ascorbic acid and the copper acetate was warmed at 50 °C to assist the dissolution of the reagents.