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Original article

A visible and long-wavelength photocured epoxy coating for stone protection

Jean-Marc Tulliani*, Chiara Letizia Serra, Marco Sangermano

Department of Applied Science and Technology, Politecnico di Torino (I), INSTM R.U PoliTO-LINCE Lab., Corso Duca degli Abruzzi 24, 10129 Torino, Italy

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ABSTRACT

An epoxy coating modified by PDMS hydroxyl terminated is presented in this paper in order to evaluate its potential use as a protective of a stone surface. With a view to its use in restoration sites, visible and long-wavelength photoinitiated cationic polymerization is proposed here. The system investigated is based on a crosslinking mechanism which shows remarkable advantages for stone protection, such as the low toxicity of the products and facility of mixture preparation. Furthermore, the visible light exploitation represents the most important advantage, because it is easy to apply in a restoration site, with or without irradiation instruments. Besides coating characterization through FT-IR, DMTA analyses and contact angle measurement on glass slides, analyses were also carried out on coated plaster samples. These analyses were performed in order to evaluate the effectiveness of the protective, in relationship to hydrophobicity (contact angle measurement, capillary water absorption) and morphology surface changing (SE/SEM observations, colorimetric measurements) before and after polymer application and UV aging test of coated samples. The overall characterization makes it possible to consider it a suitable coating for stone protection.

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1. Research aims

The aim of this research is to take advantage of the good results obtained with visible and long-wavelength photoinitiated cationic polymerization, to introduce this process into the conservation field. In fact, we considered that some of the benefits that this polymerization process has shown in another sector, such as the absence of any solvent and the easy *in situ* mixture and application, could also be successfully exploited with a modified epoxy resin to develop new protectives for stones.

2. Introduction

It is a well-known fact that stone protection in the field of cultural heritage represents an intricate challenge, because of the difficulty to meet all the criteria required. In fact, an ideal coating should be efficient, stable, durable, transparent, easy and safe during application and removal [1]. Moreover, the protective coating should guarantee a high level of hydrophobicity, considering that rain water represents the main medium for degradation mechanisms [2]. Nevertheless, *transpirability*, or rather water vapor transmission, should be guaranteed, allowing the removal of water due to rain or capillary rise [3]. Silicone resins and acrylic-fluorinated compounds are the products most commonly proposed as protective coating [4–7]. Silicones and especially acrylic resins have been widely used in the restoration field also for other kinds of interventions, such as consolidation treatments [8].

On the contrary, epoxy resins have been considered *dangerous* for a long time, due to some inherent features namely stiffness, yellowing and low reversibility (or better retreatability) [9,10]. Thus, applications for aesthetic reasons have been totally banned. Further studies have demonstrated that yellowing processes are due to the presence of chromophores groups, but as with other polymers, the choice of the epoxy system together with the means of application and post application conditions have a strong influence on the results [11]. On this basis, interesting studies have been carried out over the past years also on epoxy resin systems, especially on cycloaliphatic epoxy resins as consolidant treatment for stone conservation [12–14]. Yellowing which can be ascribed to the aromatic moieties of bis-phenol-A based epoxy monomers usually employed, can be avoided using a cycloaliphatic monomer.

The system presented here is a visible and long-wavelength photoinitiated cationic polymerization of a dicycloaliphatic epoxy resin (CE) and a diglycidyl ether (HDGE) cured in the presence of a polysiloxane hydroxyl terminated oligomer (PDMS-OH) as an additive. On the basis of some of our previous studies [15,16], this system has been specifically developed and tested for its feasibility for stone protection, with conservation criteria as the main goal. For

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* Corresponding author. Tel.: +390110904700; +390110904624.
E-mail addresses: jeanmarc.tulliani@polito.it (J.-M. Tulliani), chiaraletizia.serra@polito.it (C.L. Serra), marco.sangermano@polito.it (M. Sangermano).

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this reason, the addition of HDGE as the reactive diluent was tested to flexibilize the polymer, in compliance with conservation requirements [17]. The addition of an appropriate amount of PDMS-OH was tested as both hydrophobic and rheological controller, keeping the protective coating on the surface.

Few applications of the photopolimerization process have been exploited in the stone protection field. A photo-curing system has been recently studied, but it concerns a radical UV-cured siloxane-modified acrylic coating [18,19]. Due to its advantages, the UV curing process is widely used in different fields, such as solvent-free formulations and lower energy required with respect to thermal curing [20]. In particular, the cationic photopolymerization presents other relevant advantages, such as avoiding the oxygen inhibition, and uses monomers that are less toxic and irritant than the acrylic monomers in radical processes.

Cationic curing polymerization is a multistep process that starts with the photoexcitation of dyaryliodonium or triarylsulfonium salts, followed by the decay of the resulting excited singlet state with both, heterolytic and homolytic cleavages. The initiator of cationic polymerization is the Brønsted acid generated by a reaction among the very reactive cations and aryl-cations with monomers. Initiation of polymerization takes place by protonation of the epoxy monomer, and then by the addition of further monomer molecules through a chain growth reaction [21]. In this work, the PDMS-OH was added to the formulation and thus, the so-called activated monomer (AM) mechanism took place together with the usual mechanism for the ring-opening polymerization of epoxies known as ACE (Activated Chain-End Mechanism) [22]. The AM mechanism is active when the cationic polymerization of epoxies is carried out in the presence of alcohols. In our case, this was achieved through the PDMS hydroxyl terminated. During the polymerization, the growing ionic chain end undergoes a nucleophilic attack by the alcohol to give a protonated ether. Deprotonation of this ether by the epoxy monomers results in the termination of the growing chain and the proton transfer to the monomer can start a new chain. The polymer now has an alcohol fragment as an end group. As a consequence of the chain transfer reaction, there is an increase of flexibilization of the cured film with a consequent delay in vitrification.

Several studies have been carried out on dyaryliodonium or triarylsulfonium photoiniators salts, in order to extend their absorption bands, because they have their principal absorption bands in the short-wavelength (220–310 nm) region of the UV spectrum. The number of photosensitizers operative in the long wavelength are limited and, generally, they suffer from poor solubility in a wide variety of monomers. Therefore, in our investigation, we selected the so-called free-radical promoted cationic polymerization to extend the wavelength range of onium salt photodecomposition by using camphorquinone (CQ) as previously reported [23–25]. These free-radicals can be produced by using CQ which exhibits a strong absorption in the wavelength region between 420 and 500 nm. The choice of this compound was made on the basis of its high absorption coefficient and long-wavelength absorption as well as its excellent solubility and low toxicity. Camphorquinone is well known to undergo n-p* excitation on long-wavelength irradiation and to initially generate the excited singlet state that rapidly undergoes efficient intersystem crossing to the excited triplet. Due to the diradical character, there is a strong tendency for excited triplet carbonyls to abstract hydrogen atoms from an appropriate donor, in our case the monomer itself. At this point, the onium salt can oxidize this carbon-centered radical. The generation of an aryl radical by the decomposition of the diaryliodide free radical closes the cycle by providing a species that again can abstract a hydrogen atom from the monomer. Carbocation is formed and it is reactive enough to start the cationic ring opening polymerization.

The epoxy system investigated in this paper was cured by using a long wavelength emission lamp in order to simulate solar-light emission in the laboratory. The curing conditions were studied and the protective coating fully characterized.

Finally, the effect of natural light on the developed composition was checked through the outdoor exposition of a few samples during favorable environmental conditions. It was verified that the cationic photopolymerization was effective, since the gel content was close to the values measured for the samples polymerized by means of the lamp (data not reported).

3. Experimental

3.1. Materials

The bis(cycloaliphatic) diepoxy resin 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexyl carboxylate (CE), the hydroxy-terminated PDMS (viscosity of 1,800–2,200 cSt), as the cationic photoinizator, triphenyliodonium hexafluoroantimonate (PI) and the photosensitiziers 2,3-bornadione (Camphorquinone, CQ), were purchased from Sigma-Aldrich (Milan, Italy). The 1,6-hexanediol diglycidyl ether (HDGE) was purchased from EMS (Switzerland). All the products were used as received without any further purification.

In the frame of the more general research project “Re-frescoes” [26,27], the so-called artificial stones [28] as plaster samples were formulated in our laboratory and employed to test the protective efficiency. A magnesian lime has been purchased from La Calce del Brenta (Padua, Italy) and employed as slaked. Its water content is 50 wt%. Silica sands have been employed as aggregates with the following grading curve: 15% (0.075–0.150 mm), 25% 0.150–0.300 mm, 35% (0.300–0.600 mm), 25% (0.600–1.120 mm). They were sampled from the Sesia river (Varallo, Italy). The binder/aggregates ratio was 1:3 in volume. The plaster specimens ($5 \times 5 \times 2\,cm^3$) were slightly polished using carborundum paper of 400 mesh in order to reduce the degree of roughness preparatory for contact angle measurement. They were then washed with water, dried in an oven at 60 °C and kept to constant weight in a dryer.

3.2. Preparation methods

The photocurable formulations were prepared by mixing CE and HDGE in 1:1 molar ratio. Different amounts of the siloxane additive were added to the epoxy resins in the range between 2–8 per hundred resin (phr). The cationic photoiniziator (PI) and the photosensitizier (CQ) were added in 0.5 and 4 phr respectively. The formulations were coated both on glass slides by means of a wire-wound applicator and on one of the wider surfaces of the plaster samples by brush. The average amount of polymer applied range from 0.48 to 0.64 mg/cm^2 (determined by weight difference). Then, the prepared samples were exposed to visible light irradiation by using a lamp set up as follows: six neon lamps purchased from Osram were placed inside a plastic box (generally used for electric panel) of standard dimensions ($50 \times 30\ cm^2$) at a regular distance of 5 cm to each other. The radiation intensity was approximated to be $134\,mW{\cdot}cm^{-2}$, assuming a point source lamp and considering the following selected parameters to achieve a comparable intensity with standard instruments: the distance between samples and lamps (4 cm), the power of each lamp (9 W) and the placing of each sample regularly under the box, in order to be irradiated homogeneously by the three lamps. Moreover, this lamp was selected for its spectrum emission, especially for its maximum wavelength equals to 435 nm, close to the CQ λ_{max} absorption of 478 nm, to optimize the light absorption and the curing process consequently.

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