Science of the Total Environment 645 (2018) 817–826

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Analytical assessment to develop innovative nanostructured BPA-free epoxy-silica resins as multifunctional stone conservation materials

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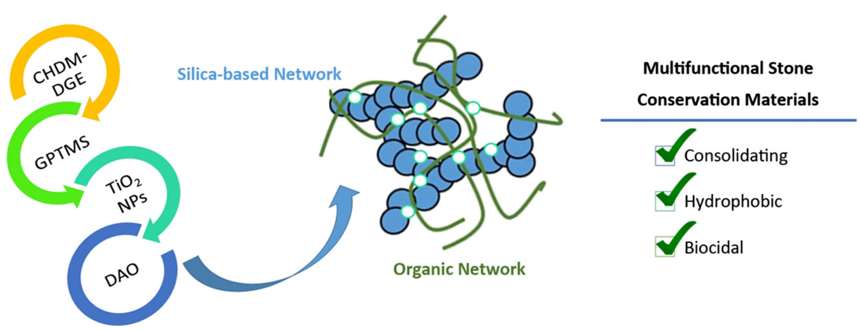
HIGHLIGHTS

- Sustainable BPA-free epoxy-silica resins for stone conservation from CHDM-DGE
- Raman spectroscopy as a powerful tool to monitor the reactions
- GPTMS as coupling agent to enhance the organic/inorganic interphase bonding

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 April 2018
Received in revised form 2 July 2018
Accepted 14 July 2018
Available online xxxx

Keywords:
Hybrid materials
Epoxy resins
Nanotechnology
Conservation
Alkoxysilanes
BPA-free

ABSTRACT

Bisphenol A (BPA)-free epoxy resins, synthesized from low molecular weight cycloaliphatic compounds, may represents promising materials for stone conservation due to their very appealing and tunable physico-chemical properties, such as viscosity, curing rate and penetration ability, being also easy to apply and handle. Furthermore, alkoxysilanes have been widely employed as inorganic strengtheners since they are easily hydrolysed inside lithic substrates affording Si—O linkages with the stone matrix. Taking into account the advantages of these two classes of materials, this work has been focused on the development of innovative conservation materials, based on hybrid epoxy-silica BPA-free resins obtained by reaction of 1,4-cycloexanedimethanol diglycidylether (CHDM-DGE) with various siloxane precursors, i.e. glycidoxypropylmethyldiethoxysilane (GPTMS), tetraethyl orthosilicate (TEOS) and isobutyltrimethoxysilane (iBuTMS), using the 1,8-diaminooctane (DAO) as epoxy hardener. Thanks to Raman spectroscopy the synthesis processes have been successfully monitored, allowing the identification of oxirane rings opening as well as the formation of the cross-linked organic-inorganic networks. In accordance with the spectroscopic data, the thermal studies carried out by TGA and DSC techniques have pointed that GPTMS is a suitable siloxane precursor to synthesize the most stable samples against temperature degradation. GPTMS-containing resins have also shown good performances in the dynamic mechanical analysis (DMA) and in contact angle investigations, with values indicating considerable hydrophobic properties. SEM analyses have highlighted a great homogeneity over the entire observed areas, without formations of clusters and/or aggregates bigger than 45 μm, for the cited materials, confirming the efficiency of GPTMS as coupling agent to enhance the organic/inorganic interphase bonding. The variations provided by the incorporation of nanostructured titania, specifically synthesized, inside the epoxy-silica hybrids have been also

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https://doi.org/10.1016/j.scitotenv.2018.07.188

evaluated. According to all the collected results, the hybrid materials here reported have proven to be promising multifunctional products for potential application in the field of stone conservation.

1. Introduction

Historical lithic materials are exposed to a permanent and irreversible deterioration induced by various physical, chemical and biological processes, both of natural and anthropogenic origin. The efforts made by the scientific community to face this problem have clarified the chemical reactions occurring between the stone materials and the exposure environment, establishing also the processes responsible for the different degradation phenomena that affect the long-term conservation of stone (Doehne & Price, 2010). Once the weathering has started, the stones should be treated with products able to improve their resistance against decay, by the employment of formulations with consolidating, water repellent and biocidal properties. Accordingly, these materials should ensure good adhesion and intergranular cohesion within the lithic matrix, as well as the protection of the stone against the harmful action of water, atmospheric pollutants, particulate matter and thermal stress, among others (Princi, 2014; Gómez Laserna et al., 2013; Gómez Laserna et al., 2015). In addition, the design of advanced conservation products requires compliance with eco-sustainability criteria. This point is crucial, not only to respect the health and the environment, but also to avoid the drawbacks arising from the use of non-tested materials as found for several products largely employed in the past for restoration activities. In this sense, during the last decades, different conservation materials have been employed, which partially fulfill the above conditions. Among the most common organic polymers used in conservation it is worth to mention acrylic polymers, epoxy resins, polyurethanes and perfluoropolyethers (Doehne & Price, 2010). In general, they display good hydrophobic properties and, some of them, also consolidating capability. However, in the long term, their thermal and photochemical instability cause chromatic and mechanical alterations (Sadat-Shojai & Ershad-Langroudi, 2009). In contrast, silica-based materials obtained from alkoxysilanes and alkylalkoxysilanes in situ sol-gel reactions solve the above drawbacks, although they often display cracking upon drying thus reducing the consolidation efficiency and, due to their structural rigidity, show mechanical properties which are not compatible with the ones of weathered stones; in addition, the low molecular weight starting compounds are prone to evaporation before the polymerization process occurs inside the stone substrate (Scherer & Wheeler, 2009; Cardiano et al., 2003a).

Nevertheless, a synthetic strategy can be adopted to overcome the limits featuring the materials used in stone conservation treatments; it consists in the development of organic-inorganic hybrid materials properly designed to minimize, as much as possible, the drawbacks connected to the employment of pure organic and inorganic materials (Kickelbick, 2014; Cardiano et al., 2003b; Cardiano et al., 2005). In this sense, epoxy resins display a set of characteristics such as good adhesive properties, high chemical resistance, in situ applicability and easy processability turning out to be highly attractive materials in the field of stone conservation (Jin, 2015). The synthesis of common epoxy resins has been developed on the use of Bisphenol A (BPA)-based diglycidyl ethers for the high reactivity of their oxirane groups towards nucleophilic compounds. However, due to the growing awareness of the influence of aromatic compounds on public health, as well as for the BPA similarity to estrogen 17beta-estradiol, imparting it the ability to act as an endocrine disruptor, their use has been discouraged (Chapin et al., 2008; Al-Saleh et al., 2017).

Taking into account all of the above, the main objective of this work has been the development of innovative conservation products, based on new BPA-free epoxy-silica hybrid materials, that could combine the advantages coming from the use of both organic (flexibility, processability, hydrophobicity, etc.) and inorganic (high mechanical strength, good chemical resistance, thermal stability, etc.) materials for stone protection and consolidation.

For that purpose, 1,4 cyclohexanedimethanol diglycidyl ether (CHDM-DGE) has been selected as epoxy precursor to synthesize hybrid materials with suitable conservation properties, thanks to the insertion of low molecular weight silica precursors within the organic network through sol-gel technology (Pandey & Mishra, 2011). CHDM-DGE is characterized by two oxirane rings and, therefore, may provide a high degree of cross-linking to develop a series of resins that should display mechanical and thermal properties comparable to the ones featuring the conventional epoxy materials, based on Bisphenol A, such as 4,4′ isopropylidenediphenol diglycidyl ether (DGEBA). On the other hand, since CHDM-DGE is not an aromatic derivative, it can display the double advantage of being a more "sustainable" starting material, thus avoiding risks for human health and environment deriving from its use and, at the same time, less prone to yellowing. The absence of aromatic rings makes the resulting resins UV resistant and suitable for outdoor applications, while also reducing their viscosity, being the yellowing and the exfoliation due to sun rays the main drawbacks connected with DGEBA use in stone conservation (Cardiano, 2008). Since the properties of organic/inorganic hybrid networks strongly depend on the degree of phases dispersion which is, on turn, a function of various synthetic parameters (i.e. stoichiometric ratios, number of reactive groups, reactivity of cross-linking reagents, etc.), the epoxy-precursor has been cross-linked with a selected hardener, 1,8 diaminooctane (DAO), in the presence of different amounts of a series of silica-forming co-reactants, i.e. tetraethyl orthosilicate (TEOS), isobutyltrimethoxysilane (iBuTMS) and glycidoxypropylmethyldiethoxysilane (GPTMS) (Fig. 1).

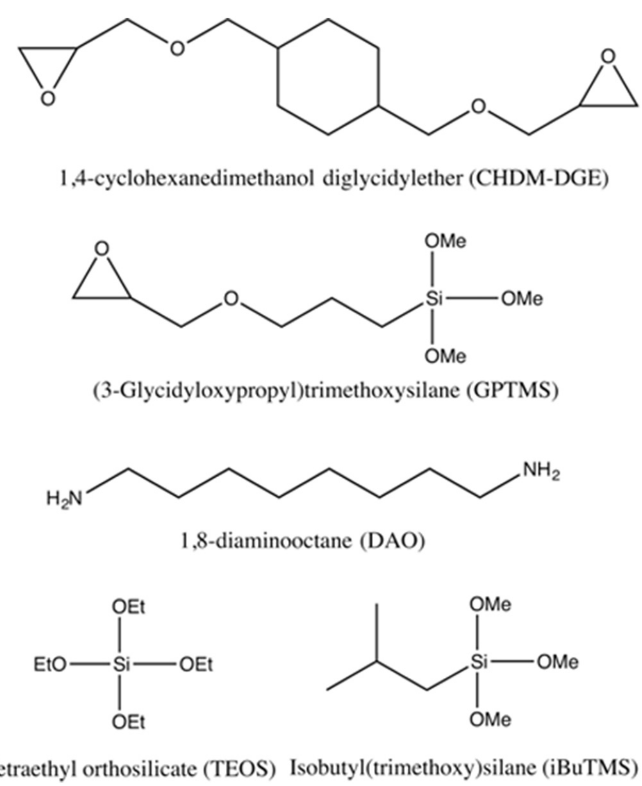

Fig. 1. Reactants employed for the epoxy-silica hybrids syntheses.