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Original article

Investigation on the chemical structure and ageing transformations of the cycloaliphatic epoxy resin EP2101 used as stone consolidant

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ABSTRACT

The commercial cycloaliphatic epoxy resin EP2101, frequently used as a structural stone strengthening agent in monuments, was tested to ascertain the related chemical nature, the mechanisms involved in the polymerization reaction and the stability under degradative environments. After a preliminary chemical characterization in the laboratory by means of GC/MS and FTIR, the resin was applied by brushing to the surface of veined Carrara marble and Vicenza white limestone specimens, and subjected to three different typologies of degradation: natural weathering, artificial accelerated ageing and resistance to mould growth. The resin's stability was monitored by microscopic observations, FTIR and SEM-EDX analysis, colorimetric and water absorption measurements. The results prompted a number of considerations, which were confirmed by those obtained from the examination of samples taken from a granite column in Murano (Venice) and a laboratory specimen of Proconnesian marble, treated in 1985 and 1984 respectively.

1. Introduction

Epoxy resins were produced in the late 1940s and were soon after adopted for use in the conservation of stone materials [1,2]. Their superior physico-mechanical properties and various cross-linking possibilities [3,4] make them reactive thermosetting polymers with multiple technical applications. In general, they have good resistance to chemical agents (especially to alkali) and water, but the main feature is their excellent strengthening effect and good resistance to mechanical stress further to an also good adhesion to the majority of substrates. These peculiarities encouraged the application of epoxy resins to various stone materials as stone consolidants. However, their use is limited due to their high viscosity. Good penetration requires a low-viscosity formulation (< 2 mPa·s), while the lowest-molecular-weight epoxies and amines have a viscosity equal to ≈10 mPa·s [5]. Cured epoxy resins, as well as all cross-linking polymers, are insoluble in all solvents though they are swollen by some of them, thus enabling the gel produced to be removed mechanically. Moreover, other disadvantages such as brittleness, easy stress-cracking under impact and stress after curing, limit their further applications also in high-tech-fields [6,7]. In conservation, epoxy resins have been more frequently used in Eastern Europe than in Italy [7]. However, in the specific case of Venice, several commercial epoxy resins, based on bisphenol A diglycidyl ether (DGEBA), have been tested and applied on monumental buildings. In 1972, the aromatic product Maraset X555 (hardener H555), by Maraglass Corp, was successfully applied for the consolidation of the statue of Madonna con Bambino (G. Lascaris) on the main façade of the Church of S. Maria dei Miracoli [8]. In 1972–1975 Araldite AY 103, by Ciba Geigy S.p.A, catalyzed with the hardener HY 951, was used for the protection of the rosso di Verona limestone of the Loggetta del Sansovino (at the bottom of the bell tower of the St. Mark's Basilica), but the results were considered unsatisfactory. In fact, aromatic DGEBAs are prone to degradation and yellowing by light, ultraviolet absorption and heat. In general, analytical tests demonstrated that the yellowing effect can be attributed to the photo-degradation of the amine hardener [9], to the degradation of additives [10] or to the chemical composition of the resin [11].

Moreover, the aromatic nature of the compound confers a molecular rigidity that results in increasing resin viscosity and a consequent low penetration depth in porous substrates. It is for these reasons that they were more widely used as a mortar binder in order to fill cavities, cracks, or as a structural adhesive. The transformation of the aromatic structure into an aliphatic derivative by hydrogenation yielded a polymer with much lower viscosity. It also provided a resin that was less likely to discolor, more stable

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Fig. 1. State of conservation of an ancient Mysian granite column on the Island of Murano before consolidation treatment (A) and the trakyte Gatta di Sant'Andrea in Padua before (B) and after (C) restoration using EP2101.

to weathering and less sensitive to hydrolysis [12,13]. Anyway, cyclo-alyphatic epoxy compound may suffer photo-alteration like most organic polymers. In particular, previous studies suggested that polymers photo-degradation generates carbonyl and hydroxyl groups through chain scission and hydrogen abstraction from the polymer backbone [14–16]. The generating of olefinic species and, in particular, the formation of conjugated C=C and C=O, contribute to the discoloration of the polymer [17]. In Italy, a cycloaliphatic epoxy resin monomer of undisclosed structure designated EP 2101, was marketed by the company STAC of Milan (Italy). Right away, it was tested by laboratory application on different stone substrates, and its stability to UV radiation was judged very promising and comparable to acrylic resins [18,19]. Moreover, it seemed that EP2101 could substantially improve the mechanical resistance of various heavily deteriorated stone types.

A number of architectural stone elements showing strong decay morphologies were therefore treated with EP 2101. Fieldwork with this resin began in 1983 [20] on sections of a Roman aqueduct made of Viterbo tuff. In the following year, EP2101 was applied by direct brushing procedure to different materials of several buildings: panels of Chiampo limestone in a bell tower of Arzignano (Vicenza), four limestone window frames in the bell tower of the Church of the Natività della Beata Vergine in Trento, and the Gatta di Sant'Andrea, also known as the Venetian Lion, in Padua made of Euganean trachyte (Fig. 1), an ancient column of Turkish granite on the Island of Murano (Venice, Fig. 1) [21], an oolitic limestone panel of the Church of San Zeno in 1985 and the Arche Scaligere in red Veronese limestone (Rosso Ammonitico) in Verona, some limestone columns of the Church of S. Andrea (Mantua) and two rensed Roman granite columns in the main façade of the Cefalù Cathedral (Sicily). Today EP2101 is still available on the market and sold by the Bresciani company (Milan, Italy). As for the treatment method, the resin was initially applied by simply brushing the surfaces (e.g. in the Arzignano bell tower), then (the Murano column) by capillary impregnation using a pack made of cottonwool fixed to the shaft by cotton gauze; the best results were however obtained by vacuum impregnation after application of a cotton pack (the Cefalù columns, Fig. 2).

No datasheet was and is available to indicate the chemical composition of the resin actually used, and its specific features remain unclear. Moreover, no studies have been carried out to illustrate the mechanisms of the polymerization process or the relative behavior and stability over time. Assessing the resistance of a protective or strengthening agent to natural weathering or to microbiological attack, is typically a lengthy process necessitating long-term field trials. However, the knowledge of the mechanisms of alteration allows for better understanding of the needs, purposes, and limits of the different conservation treatments.

For these reasons, this study aims at a better understanding of the chemical nature and stability of EP2101 after natural and artificial ageing. After a preliminary chemical characterization in the laboratory, the resin was applied to veined Carrara marble and Vicenza white limestone specimens, and subjected to three different typologies of degradation: natural weathering in Venice, artificial ageing (xenon irradiation) and resistance to mould growth. Gas chromatography coupled with mass spectrometry (GC/MS) and Fourier transform infrared spectroscopy (FTIR) were of invaluable help in identifying the chemical characteristics and features of the resin, and in understanding the sol-gel processes and the polymer structural changes due to artificial irradiation and natural weathering. Microscopic observations of cross-sectioned samples (especially by means of SEM-EDX analysis) were carried out to investigate the morphology of the stone after the application of the resin, as well as to ascertain the presence of biological colonization. In addition, colorimetric and water absorption measurements (sponge-contact method), were used to verify chromatic alterations and variations of water repellency of the treated surfaces, connected to the degradation of the polymer.

2. Materials and methods

2.1. Materials

The commercial product tested was the epoxy resin EP2101, marketed by the Italian company Bresciani and produced by the