Construction and Building Materials 161 (2018) 618–633

Contents lists available at ScienceDirect

Construction and Building Materials

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

Durability of an epoxy adhesive used in civil structural applications

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HIGHLIGHTS

- The durability of a cold-curing structural epoxy adhesive was addressed.
- Effects of hygrothermal and outdoor ageing were studied for up to two years.
- Media diffusion, and viscoelastic and mechanical behaviour were characterised.
- The water uptake did not follow a Fickian behaviour.
- Both viscoelastic and mechanical behaviour showed irreversible degradation.

ARTICLE INFO

Article history:
Received 31 October 2017
Received in revised form 28 November 2017
Accepted 30 November 2017

Keywords:
Structural adhesive
Epoxy
Durability
Hygrothermal ageing
Outdoor ageing

ABSTRACT

This paper presents an experimental study about the durability of a cold curing structural epoxy (EP) adhesive exposed to different hygrothermal and outdoor ageing environments, typical of civil engineering applications, for up to two years: water and salt water immersion at 20 °C and 40 °C, continuous condensation at 40 °C, and outdoor ageing in a mild Mediterranean climate. After specific exposure periods, changes in the following physical properties and mechanical behaviour of the adhesive were assessed: (i) media diffusion, through water uptake (in hygrothermal environments); (ii) viscoelastic behaviour, through dynamic mechanical analyses (DMA); and (iii) flexural and (iv) in plane shear behaviour. Regarding media diffusion, water uptake did not follow a Fickian behaviour and a final saturation stage was not reached; two alternative non-Fickian analytical models were successfully fitted to the test data and the corresponding diffusion parameters were determined. In what concerns the viscoelastic behaviour, while continuous condensation and outdoor ageing caused negligible changes, the T_g of the adhesive generally decreased due to immersion (around 20% in water and 10% in salt water after two years); in addition, at later stages of water immersion, the $\tan\delta$ curve showed significant shape differences, with the usual curve peak being replaced by two different peaks; a generalised reduction of the storage modulus at the glassy plateau was also noted. In terms of mechanical performance, such plasticization effects were visible in the flexural and shear stress-strain behaviours. The flexural properties exhibited irreversible degradation, with the highest reductions (two years of ageing in water at 40 °C) being about 24% and 30% in strength and modulus, respectively. Regarding the shear properties, in hygrothermal environments the shear modulus showed similar decreasing trends to the flexural modulus (43% reduction after one year), but the shear strength increased (~25%); the outdoor ageing affected the shear properties in the same way, but the magnitudes of the changes were lower.

1. Introduction

Bonding operations in building and bridge construction are often performed outdoors, sometimes involving large bonding areas. This explains why ambient cured thermosetting resins, namely epoxies, are generally selected for this purpose [1]. The increasing interest in epoxy adhesives also stems from the many formulations available, which provide a wide range of properties (before and after curing) that make them suitable for bonding different substrate materials in a broad variety of applications and conditions; the usual range of operating temperatures and the limited cure shrinkage of epoxies also favour their use in civil engineering [2,3].

However, the use of adhesive bonding in civil engineering entails several challenges, some of which are related to the

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https://doi.org/10.1016/j.conbuildmat.2017.11.168
0950-0618/

adhesives themselves and their durability, as the joint reliability is very much dependent on the bonding agent [4]. The effects of environmental agents on structural adhesives, such as moisture and temperature, have been considered as the most relevant factors concerning their long-term performance [3,5,6]. In fact, in several civil engineering applications, bonded joints can be exposed to moisture or humid environments [7].

As mentioned, the exposure temperature is an important environmental factor that limits the application range of structural adhesives. Temperatures that approach or exceed the glass transition temperature (T_g) of the adhesive promote significant changes in the material behaviour, which may change from hard to rubbery, thus limiting its applicability [8]. The temperature during the application is also very relevant for the curing degree and mechanical properties attained by structural adhesives. In fact, exposure to low or elevated temperature (the first typically delays curing, while the latter is often used to accelerate it) can cause positive or negative changes in strength and stiffness, depending on the magnitude and duration of the temperatures experienced by the adhesive [9,10].

Another important factor is concerned with moisture. Water diffusion in adhesives, which is intrinsically related to their polymeric structure, can be influenced by their chemical composition [11], topology, polarity and molecular motions [12], with water molecules being usually classified into free water (isolated) and bound water (*i.e.*, linked to the epoxy [13]). Once absorbed by epoxy, water can change its properties through plasticization (reversible), hydrolysis, cracking or crazing (irreversible) [1]. The physical and chemical transformations experienced by epoxies in the presence of water cause detrimental effects, namely reductions of the T_g and of the mechanical strength [14].

The information about the long-term behaviour of bonded joints in building or bridge construction is limited, and the same applies to the durability of epoxy adhesives, revised in the next section. The availability of such information is of paramount importance, since the required service life for most civil engineering applications is generally above 50 years. This lack of experimental data about the durability of joints and adhesives (needed for design) is one of the aspects that is hindering the widespread dissemination of this connection technology.

Other industries, such as aerospace and electronics, have longer experience in studying the effects of ageing on epoxy adhesives [3,15]. However, the results obtained are hardly useful for civil engineering applications, given the many differences between those industries, namely (i) the loading conditions, (ii) the types of environmental exposure, (iii) the substrate materials and manufacturing processes, and (iv) the service life requirements.

To address these issues, this work aims at assessing the influence of different ageing conditions, representative of civil engineering environments, on the durability of a commercial epoxy adhesive used in structural applications. In particular, the effects of immersion in water and salt-water at 20 °C and 40 °C, continuous condensation at 40 °C and outdoor exposure for up to two years on the physical, viscoelastic and mechanical properties of the adhesive were determined.

2. Literature review

This section presents a literature review of previous studies about the effects of hygrothermal and outdoor ageing on epoxy adhesives. The review, summarized in Table 1, focused on how different types of hygrothermal and outdoor ageing environments affect the properties of epoxy adhesive systems[1] likely to be used in civil engineering structural applications. However, it is worth referring that the formulation of the adhesives used in the studies may differ, as well as the curing/conditioning conditions employed before testing, and such differences can influence their behaviour and susceptibility to external factors.

2.1. Hygrothermal ageing

Zhou and Lucas [16,17] investigated the nature of absorbed water and the hygrothermal effects in the T_g of three different thermoset epoxy systems immersed in water at different temperatures (45 °C–90 °C). The authors concluded that changes in the T_g did not depend only on the water content, but also on the hygrothermal history of the polymers (both time- and temperature-dependent). After an initial reduction, the T_g began to gradually recover with time after reaching the saturation stage, with higher immersion periods and temperatures resulting in higher recovery values. However, the residual T_g after immersion still showed a significant reduction compared to the unaged condition – at 45 °C it ranged from 54% to 65%, at 60 °C it was around 43% to 57%, and at 90 °C it varied between 28% and 48% for the three epoxy systems.

Nogueira et al. [18] studied the effect of water sorption at 100 °C in an amine-cured epoxy system and noticed that the T_g continuously decreased as the absorbed water increased – reductions of 16% and 6% (depending on the pre-curing conditions) were noted on fully saturated specimens, which were much lower than those reported in the study by Zhou and Lucas [17] for a similar duration and temperature of immersion. Mechanical properties were also affected: the tensile strength exhibited a global decreasing trend, especially in the earlier stages of diffusion, with a 33% reduction for the last immersion period (55 days); after an initial increase, the tensile modulus also showed a general reduction trend, yet with a much lower magnitude – 5% reduction at the later stages.

Frigione et al. [19] obtained similar results in another particular epoxy system. The specimens were immersed in water and subjected to water vapour (100% relative humidity, RH) for 28 days (about half of the time of the previous studies) at 23 °C (lower than in earlier studies). Both types of hygrothermal ageing caused moderate to low reductions in performance: 14% (water vapour) and 16% (water immersion) in flexural modulus; 1% and 4% in flexural strength, and 1% and 5% in T_g, respectively. The authors highlighted that the 28 days exposure period was too short to induce irreversible degradation to the adhesive; in any case, unlike the previous work [18], the modulus seemed to be more affected than strength. In this study, specimens were also exposed to 50 °C for 28 days: the thermal exposure led to a 15% increase of the T_g, due to density increase of crosslinking. For this exposure the flexural strength increased 32% (due to the same effect), but the flexural modulus was reduced by 19%, which was attributed to a detrimental effect (not specified) of the post curing process.

Yang et al. [20] assessed the response of an ambient cured epoxy adhesive when exposed to a variety of immersion environments over 24 months: (i) deionized water immersion at 23 °C, 38 °C and 60 °C, (ii) salt-water (5% NaCl) immersion at 23 °C, and (iii) alkaline immersion at 23 °C. Regarding the viscoelastic response of the adhesive, specimens immersed at 23 °C registered small reductions in T_g for the first 6 months, after which only insignificant changes were reported. For the 38 °C and 60 °C immersions, a 9% increase in T_g was observed in the same period, which was then levelled off after very small reductions; in addition, for higher immersion temperatures the loss factor curves showed a split in the tan δ peaks The authors concluded that the initial post-cure due to elevated temperatures dominated over the plasticization. The immersion in deionized water caused a significant decrease in tensile properties. After 24 months at 23 °C, 38 °C and 60 °C, the tensile strength and the tensile modulus exhib-

[1] This review focused only on epoxy adhesive systems, excluding adhesives with other material combinations (e.g., reinforced polymer matrixes).