Construction and Building Materials 140 (2017) 552–561

Contents lists available at ScienceDirect

Construction and Building Materials

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

Effects of aging in dry environment on physical and mechanical properties of a cold-curing structural epoxy adhesive for bridge construction

M. Savvilotidou [a], A.P. Vassilopoulos [a], M. Frigione [b], T. Keller [a,*]

[a] *Composite Construction Laboratory (CCLab), École Polytechnique Fédérale de Lausanne (EPFL), Station 16, Bâtiment BP, CH-1015 Lausanne, Switzerland*
[b] *Department of Engineering for Innovation, University of Salento, Via per Monteroni, IT-73100 Lecce, Italy*

HIGHLIGHTS

- The physical and mechanical properties of a cold-curing adhesive are investigated.
- Physical aging and curing occur simultaneously during the first year.
- The properties are driven by physical aging in the earlier and curing in the later age.
- The mechanical properties converge after one year independent of curing conditions.
- The glass transition temperature however is not yet fully developed after one year.

ARTICLE INFO

Article history:
Received 26 August 2016
Received in revised form 13 February 2017
Accepted 14 February 2017

Keywords:
Adhesive
Bridge construction
Cold-curing
Cross-link
Density
Epoxy
Physical aging

ABSTRACT

The effect of physical aging and continuation of curing on the physical and mechanical properties of a commercial cold-curing structural epoxy adhesive used in bridge construction has been investigated during the first year. Since adhesive bridge joints are sealed, only dry conditions were taken into account. Predominant physical aging in the earlier age and predominant curing in the later age affected the physical and mechanical properties. The E-modulus exhibited a maximum in the earlier age due to a maximum mass density caused by physical aging. In the later age, when curing became predominant, mass density and thus the E-modulus decreased while the cross-link density increased. After the first week, the E-modulus development became independent of the curing conditions. Tensile strength and failure strain depended mainly on the cross-link density and their development was thus influenced by the curing conditions but delayed in the earlier age due to physical aging.

1. Introduction

Structural adhesives have been used in bridge construction for strengthening purposes for decades, e.g. for bonding carbon fiber-reinforced polymer (CFRP) plates or strips onto existing structures. A more widespread application in new construction however is still restricted due to a lack of knowledge concerning their long-term mechanical behavior over a required service life of up to 100 years [1]. Structural adhesives used in bridge construction are in most cases applied on the construction site and are thus mainly cold-curing systems based on thermosetting epoxy resins. Aliphatic amines are commonly used as curing agents for this purpose, since they are also able to react with epoxies at low temperatures, i.e. during winter. Covalent bonds form between the epoxide and the amine groups, resulting in a highly cross-linked, rigid and amorphous epoxy network. However, several weeks – or even months – of curing are necessary to assure a reasonably high curing degree and a moderate glass transition temperature (T_g), which is usually lower than 65 °C, particularly if bonding occurs at low temperatures of minimum 5–10 °C [2–6].

During their service life, cold-curing epoxies are subjected to various physical and chemical aging mechanisms, which may be active simultaneously with different effects on the physical and mechanical properties, mainly depending on temperature, humidity and UV exposure [7,8]. Effects based on physical mechanisms, such as plasticization and physical aging (densification), may be reversible [3,9]; cold-curing epoxies exposed to natural weathering

---

* Corresponding author.
E-mail address: thomas.keller@epfl.ch (T. Keller).

http://dx.doi.org/10.1016/j.conbuildmat.2017.02.063

for 36 months showed partially reversible changes in both physical and mechanical properties [7]. However, effects based on chemical mechanisms, e.g. further cross-linking due to continuation of curing [2,9], or chain scissions due to long-term water attack or high temperature and UV exposure, are not reversible [7].

In bridge construction, cold-curing adhesive joints, if properly designed and executed, are normally not exposed to humidity, high temperature and UV radiation. The main aging mechanisms that still occur in such dry environments, at low or moderate outdoor temperatures (well below T_g), are physical aging and continuation of curing. In this respect however, most of the works published on physical aging concern hot-cured epoxy resins, i.e. cured at elevated temperatures (often above 100 °C) by artificial heating and works about cold- or outdoor-curing are rare [2–11]. Moreover, apart from a few works where investigations have been conducted during several months or years [3,7–9,12], most of the available studies are limited to a few days of aging. There is thus a lack of knowledge regarding the effects of physical aging and simultaneous continuation of curing on the physical and mechanical properties of cold-curing structural epoxy adhesives exposed to dry outdoor temperature conditions, as is the case in bridge applications.

Physical aging of epoxy adhesives occurs in the glassy state, i.e. after vitrification and at aging temperatures (T_a) lower than T_g, and is driven by a thermodynamic disequilibrium in this state [13]. During aging, i.e. approaching the thermodynamic equilibrium, an increase in mass density (densification), and thus a decrease in specific volume (volumetric relaxation) (v), and a decrease in molecular configurational energy are observed [3,12–16]. The difference between T_a and T_g and the thermal history have a strong influence on the rate of physical aging. If the exposure temperature is low, physical aging effects may be active for several years [3,12–14,17–21]. They may also be erased however, i.e. the adhesive is de-aged, if heating occurs at temperatures above T_g, i.e. in the rubbery state, and subsequently cooled down into the glassy state, where physical aging begins [3,14–16]. To quantify physical aging, the specific enthalpy (h) is an appropriate physical metric, since it considers both volume changes and molecular configurational changes (at constant volume) [15]. Similar to the decrease in specific volume, specific enthalpy decreases with time due to physical aging.

The interdependence of all these parameters is illustrated in Fig. 1, which shows in the upper part the specific volume (v) or specific enthalpy (h) vs. temperature (T) and in the lower part the specific heat capacity (C_p) vs. temperature (according to [15]). Indicated in the upper part are the thermodynamic equilibrium lines of an amorphous and crystalline polymer, and the region in between represents free volume. The curve v_0-h_0-t_0 describes an unaged epoxy at time t_0, either after vitrification and then heated from the glassy into the rubbery state, or hot-cured or de-aged at high temperature in the rubbery state and then cooled down into the glassy state. The curve deviates at the transition from the rubbery to the glassy state, i.e. at the glass transition temperature ($T_{g,0}$), from the amorphous equilibrium line and the adhesive thus includes additional free volume in the glassy state. At this transition, i.e. $T_{g,0}$, the specific heat capacity also increases. The unaged epoxy then starts physically aging at temperature (T_a) during the times $t_2 > t_1$, i.e. the specific volume and specific enthalpy decrease to $v_2 < v_1 < v_0$ and $h_2 < h_1 < h_0$. If the temperature subsequently increases into the rubbery state, the curves overshoot the amorphous equilibrium line, which is expressed by additional endothermic peaks in the specific heat capacity vs. temperature curves ($\Delta H_{rel,2} > \Delta H_{rel,1}$) and an increase in the glass transition temperature ($T_{g,2} > T_{g,1} > T_{g,0}$). Specific heat capacity vs. temperature curves can be obtained by Differential Scanning Calorimetry (DSC) [22]. An increasing ΔH_{rel} has been found with increasing physical aging periods of both cold-curing [3,13] and hot-cured epoxies [13,17,18].

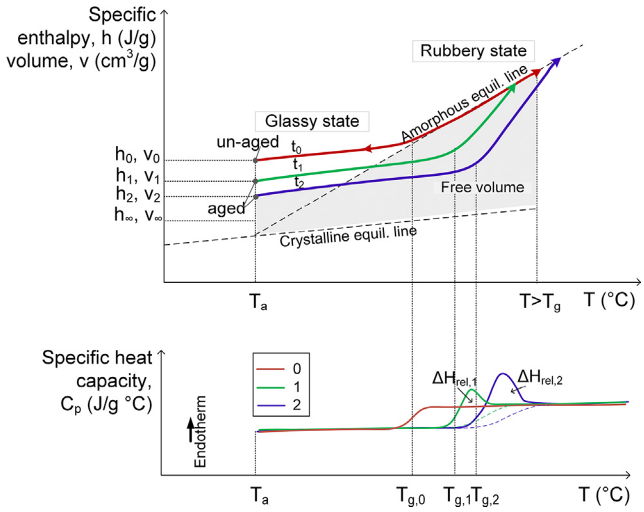

Fig. 1. Specific volume, specific enthalpy and specific heat capacity vs. temperature during heating and cooling cycles of epoxy adhesive.

Concerning the mechanical properties, since physical aging decreases the specific volume, the E-modulus increases accordingly [9,12,19]. Furthermore, the yield compressive strength increases with physical aging [17,19], while the tensile strength normally decreases as a result of the embrittlement and potential microcracking [23]. After de-aging through exposures above T_g, however, the mechanical properties almost completely recover [17].

The continuation of curing, i.e. increasing of the curing degree, in contrast to physical aging, decreases the mass density (and thus increases the specific volume) but increases the cross-link density, defined as the number of chemical cross-links per unit volume [24]. In accordance with the increase of the specific volume the E-modulus decreases during curing [12,25–29]. The glass transition temperature and strength, however, increase with increasing cross-link density, i.e. curing degree [2,10].

In this work, the physical and mechanical behaviors of cold-curing epoxy adhesive specimens are investigated during an aging period of up to 12 months in a dry environment. Post-cured epoxy specimens, i.e. heated for short times at temperatures not much higher than their T_g, are used as reference in order to derive the different behaviors at cold curing, compared to hot-cured conditions where the knowledge is much broader. The physical and mechanical property changes are discussed on the basis of the sequence or concurrence of the above-described aging mechanisms, i.e. physical aging and continuation of curing. The current work is a continuity of a previous study [2,10,11], where cold-curing structural epoxies were physically and mechanically investigated during the first ten days of isothermal curing at low temperatures (5–20 °C). Post-curing treatments had also served as reference.

2. Experimental program

2.1. Materials and conditioning

The epoxy adhesive used in this study was Sikadur-330, supplied by SIKA Schweiz AG. The primary commercial use of this cold-curing adhesive or resin is manual application to surfaces in order to bond FRP strips and impregnate FRP fabrics employed to strengthen existing concrete or steel structures. Sikadur-330 is a