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CREEP BEHAVIOR OF COLD-CURING EPOXY ADHESIVES: ANALYSIS AND PREDICTIVE APPROACH

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ABSTRACT: This study investigates the creep behavior of two commercially available cold-curing epoxy adhesives, intended for the bonding of external composite reinforcements on concrete structures. In a preliminary stage, the characteristics of the mineral fillers (nature, content and size) contained in the two systems were determined, and the viscoelastic properties of the unfilled epoxy matrices extracted from these systems were analyzed. Short-term tensile creep experiments were then carried-out on cured samples of the two adhesives and their unfilled matrices, in order to evaluate the influence of the fillers and the polymer network characteristics on the instantaneous and delayed mechanical responses. Finally, two predictive approaches based on either the Time-Temperature Superposition Principle (TTSP) or the Time-Stress Superposition Principle (TSSP) were applied to evaluate the long-term creep behavior, and their suitability in the case of cold-curing adhesives was discussed.

1. Introduction

Cold-curing epoxy adhesives are commonly used to install external fiber reinforced polymer (FRP) composite systems for repairing or upgrading reinforced concrete (RC) infrastructures. These epoxies are usually bi-components systems that contain a certain amount of mineral fillers and additives to set the rheological and mechanical properties. Their formulation is also adjusted according to the type of process intended for the installation of the FRP materials (wet lay-up, or bonding of pultruded FRP plates, for instance). For this reason, their mechanical behavior, can significantly vary from an epoxy system to another, which may affect the durability and performances of the bonded FRP reinforcement, especially under environmental ageing or sustained loads (Houhou, 2012; 2014)

In this study, it is first proposed to investigate the parameters related to the adhesive formulation (nature and content of the mineral fillers, characteristics of the polymer network) that govern the viscoelastic properties in general, and the creep behavior in particular. In this line, physicochemical characterizations are carried-out on two adhesive systems from the market, and on the unfilled epoxy binders extracted from these adhesives as well. The viscoelastic and tensile creep behaviors of the bulk adhesives cured at ambient temperature are then analyzed in the light of the previous results, in order to point out influential parameters. A second part explores two predictive approaches intended for evaluating the long-term creep behaviour, based on the Time-Temperature or Time-Stress Superposition Principles. Their suitability in the case of cold-curing adhesives, which exhibit an incomplete crosslinking, is examined.

2. Description of the selected epoxy adhesives

Two cold-curing and bi-component epoxy adhesives were selected among the various commercial products available on the French market. Both systems are used for the installation of pultruded carbon

FRP (CFRP) plates on RC concrete structures. The names of the two products are not explicitly cited in this paper, and the two systems are noted *Adhesive 1* and *Adhesive 2*.

The main physical and mechanical characteristics of these products are gathered in Table 1. The two systems contain a substantial amount of mineral fillers in their components, but the content and nature of the fillers are not mentioned in the technical data sheets.

Table 1- Properties of the two epoxy adhesives under study, as provided by the manufacturers

	Adhesive 1	Adhesive 2
Organic components	Part A: diglycidylether Bisphenol A Part B : aliphatic amines hardener	Part A: diglycidylether Bisphenol A Part B : modified polyamines and cyclo-aliphatic amines
Density at +23°C	1.65 ± 0.1 kg/l (mix A+B)	Part A : 1.43 kg/l Part B : 1.52 kg/l
Pot life in mn	120 (+8°C), 90 (+20°C), 20 (+35°C)	120 (+10°C), 60 (+23°C), 30 (35°C)
Glass transition Temp. (Tg) (ISO 11357-2)	62°C (after 7 days at +45°C)	54 ± 2°C
Tensile strength (ISO 527)	24-27 MPa (after 7 days at +15°C) 26-31 MPa (after 7 days at +35°C)	29,5 ± 1 MPa
Tensile modulus (ISO 527)	11200 MPa (at +23°C)	4940 ± 170 MPa

3. Preliminary characterizations of the adhesives

In a first step, basic characterizations were carried-out in order to:

- assess precisely the nature and content of the mineral fillers in the 2 epoxies under study,
- determine the viscoelastic properties of the cured adhesives, and that of the organic binders (*i.e.*, the epoxy matrices whose mineral fillers have been removed prior to cure). At this stage, the objective is to evaluate the influence of the fillers on the viscoelastic properties of the two commercial systems. In a further step, this will help us to understand possible differences in the experimental creep behaviors of the two products.

Observations by optical and scanning electron microscopy (SEM) techniques, coupled with energy dispersive X-ray (EDS) elemental analysis were first conducted to assess the size, the volume distribution and the nature of the mineral fillers. Fig. 1 shows polished sections of the two cured adhesives. In *Adhesive 1* (Fig. 1.a), there is a uniform distribution of large smooth particles in the polymer matrix and the largest particle sizes are around 250µm. The elemental analysis reveals that these fillers are mainly composed of silica sand. As regards *Adhesive 2*, a large density of voids can be observed (air bubbles in black on fig 1.b), and filler particles appear to be much smaller (size < 50 µm) and exhibit an elongated angular shape. In this case, EDS analyses show that these fillers consist of a mix of calcium carbonate, silica, alumina and titanium dioxide.

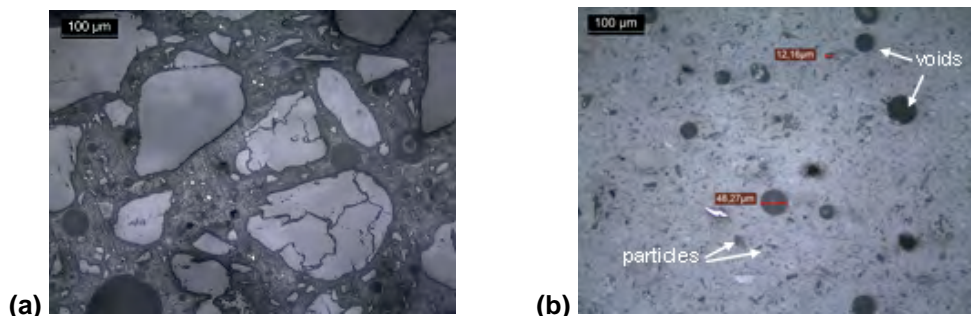


Fig. 1 - Micrographic observations of polished sections for *Adhesive 1* (a) and *Adhesive 2* (b)

The filler contents in the two pasty components (part A and B) of each adhesive were also assessed, and the global content in the mix as well (part A+ part B, according to the mix ratio recommended by the manufacturer). A centrifugation in a solution of methyl ethyl ketone (MEK) followed by a filtration made it possible to separate the organic binders from the fillers, hence to quantify their relative weight contents. Corresponding results are reported in Table 2. It was found that the filler content of *Adhesive 1* (mix A+B) is close to 80 wt.%, and much higher than that of *Adhesive 2* which is around 60 wt. %. This result is consistent with properties reported on the technical datasheet (Tab. 1), which indicate a higher density and a much higher tensile modulus for *Adhesive 1* compared to the other system.

Table 2 - Relative weight contents of organic binders and fillers in the 2 epoxy adhesives

System	Component	Organic binder (wt. %)	Filler content (wt. %)
<i>Adhesive 1</i>	A	18,4 ± 0,8	79,7 ± 0,4
	B	15,4 ± 0,8	85,2 ± 0,9
	Mix A+B (ratio 3/1)	17,7	81,1
<i>Adhesive 2</i>	A	48 ± 2	52 ± 2
	B	31 ± 2	68 ± 2
	Mix A+B (ratio 1/1)	39	60

Following the centrifugation stage, the organic binders that were extracted from components A and B of the two systems, were recombined into a mix (binder A + binder B), which was used to mold parallelepipedic samples (25mm x 4mm x 1 mm) of unfilled epoxy matrices. It is to note that the mix ratio (binder A/binder B) was recalculated, so that the stoichiometry is respected for the two systems, and the resulting samples were cured at ambient temperature for at least 1 month before further characterization. Similar specimens were produced with the filled (as received) adhesives, to serve as control samples.

Finally, the viscoelastic properties were determined by Dynamical Mechanical Analyses (DMA) for the cured samples of filled adhesives and unfilled extracted matrices. Tests were carried-out under traction/compression mode with an imposed dynamic displacement of amplitude 10 µm, at a frequency of 1 Hz. The test specimen was simultaneously subjected to a ramp of temperature between 20 and 140°C at a heating rate of 2°C/min. This technique made it possible to record the evolution of the storage modulus (E') and the loss factor ($\tan\delta$) over the temperature interval. Results are plotted in Fig. 2.

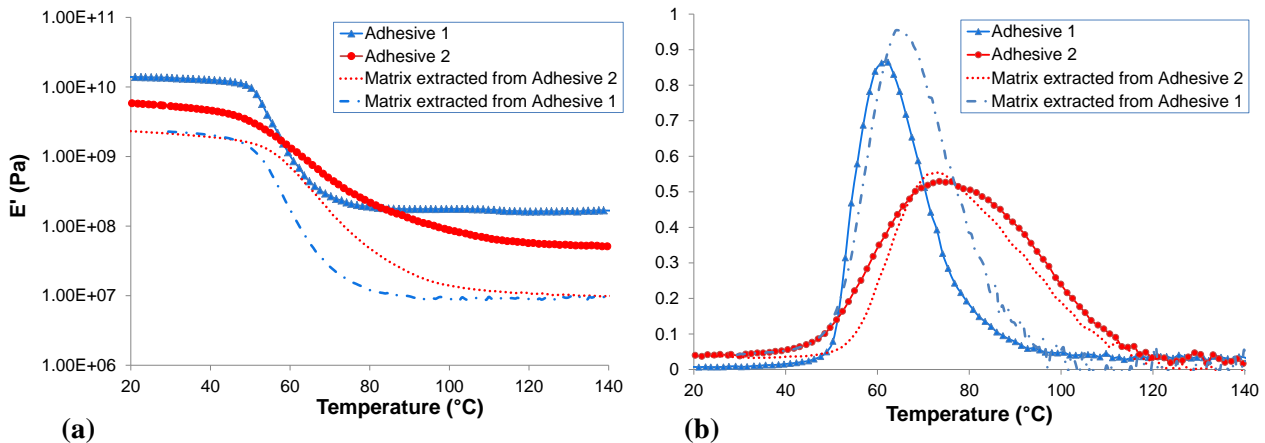


Fig. 2 - DMA experiments at 1 Hz: Evolutions of the storage Modulus E' (a) and the loss factor $\tan\delta$ (b) versus temperature, for *Adhesive 1* and *Adhesive 2* and their unfilled extracted matrices

As regards the filled adhesives, a large drop of the storage modulus is observed through the glass transition (Fig 2.a.) for both systems. However, the moduli of *Adhesive 1* in the vitreous and rubbery domains remain much higher than that of *Adhesive 2*, due the higher filler content. On Fig 2.b., the temperature at the maximum of the $\tan\delta$ peak, called T_α and closely connected to T_g , is found to be higher for *Adhesive 2* compared to *Adhesive 1* (deviation of 12°C). This feature is contradictory with the

values of T_g mentioned in the technical datasheet; which may be due to the unrepresentative cure conditions chosen by the manufacturer of *Adhesive 1* (7 days at 45°C, as reported in Table 1).

In the case of the unfilled extracted matrices, a drop of E' is also observed through the glass transition region; however, differently from the filled epoxies, the unfilled matrices extracted from *Adhesive 1* and *Adhesive 2* exhibit very similar values of the vitreous and rubbery storage moduli. This confirms the major role played by fillers on the mechanical elastic properties of commercial adhesives. As regards the loss factor peak, the matrix extracted from *Adhesive 1* exhibits lower values of both T_α and the peak amplitude, as compared to the matrix extracted from *Adhesive 2*. This feature suggests a lower crosslink density, hence a higher molecular mobility of the epoxy network in *Adhesive 1*.

Finally, DMA characterizations have shown that the elastic characteristics (storage moduli in the vitreous and rubbery domains) of the two commercial adhesives are mainly dependent on the filler content, whereas the dispersive characteristics (T_α and amplitude of the loss factor peak) are rather related to the structure of the epoxy network (nature of the reactive components, crosslink-density).

4. Analysis of the short-term creep behavior

Short-term tensile creep experiments (25°C, applied stress of 5 MPa) were carried-out on samples of the two commercial adhesives and their unfilled extracted matrices. Creep curves are displayed in Fig.3.

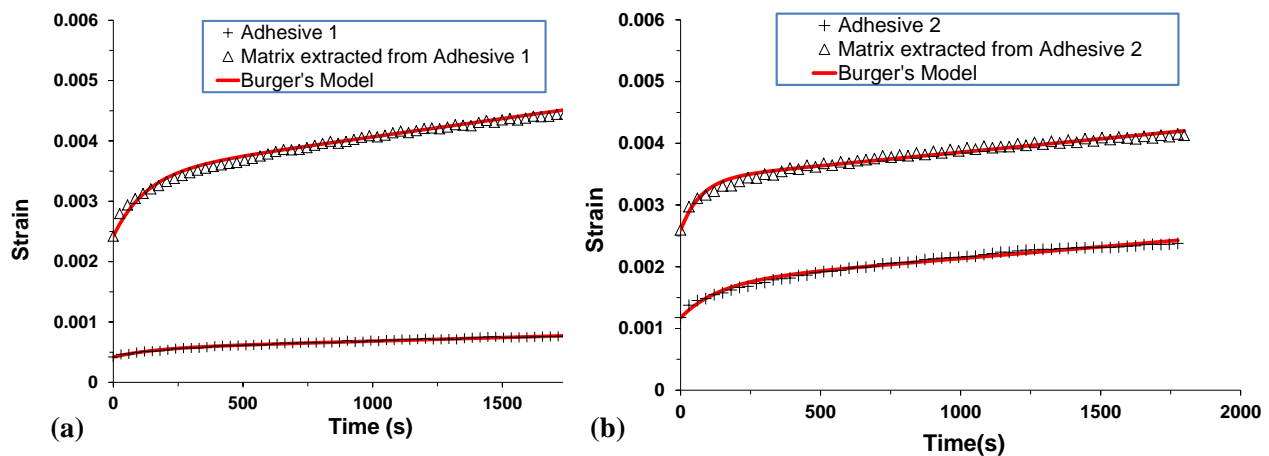


Fig. 3 - Short-term creep tests for *Adhesive 1* (a) and *Adhesive 2* (b) and their unfilled matrices, at 25°C for an applied stress of 5 MPa. Fitted curves of Burger's model are also displayed.

The two extracted matrices exhibit a similar level of elastic strain (instantaneous strain) following the initial loading stage, which is consistent with their similar storage moduli in the vitreous state. Nevertheless, matrix extracted from *Adhesive 1* presents a higher creep rate (slope of the asymptote), which can be explained by a higher molecular mobility of the epoxy network, as shown previously by DMA analyses.

Filled adhesives show globally lower levels of deformation than their extracted matrices, due to the presence of mineral fillers. When comparing the 2 filled systems together, large differences are observed in terms of initial elastic strain (it is much lower for *Adhesive 1* which has the highest filler content and vitreous elastic modulus) and in terms of creep rate (which appears higher for *Adhesive 2*). This latter result contradicts the trend observed for the extracted matrices, as the matrix of *Adhesive 1* exhibits the highest creep rate. It is thus suggested that the creep rate of filled adhesives in the vitreous state is not only dependent on the molecular mobility of the polymer matrix, but also on other factors such as interactions between filler particles. It is likely that friction phenomena between sand particles hamper the creep process in *Adhesive 1*, due to the high filler content and the large size of the sand particles.

Finally, the well-known rheological Burger's model (Fig. 4) was used to simulate the creep behaviors of both the filled adhesives and the extracted matrices. Parameters of the model were identified by fitting the experimental data, according to the method described in (Houhou et al, 2012; 2014). Values of these parameters are not reported in this paper, but it is obvious from Fig.3 that a fair agreement was obtained between experimental and modelled curves.

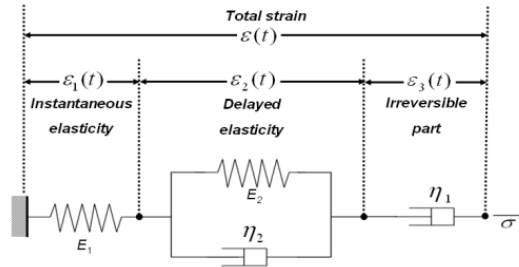


Fig. 4 - Schematic description of Burger's rheological model

5. Predictive approaches

This last part aims at comparing two predictive methods for evaluating the long-term creep response of cold curing adhesives, based on the Time Temperature Superposition Principle (TTSP) and the Time Stress Superposition Principle (TSSP). Both approaches are applied to the case of *Adhesive 1*.

The TTSP method consists in conducting short-term creep experiments at various temperatures and build a creep compliance master curve by shifting the experimental compliance curves horizontally along the log-time scale axis, so that they fit the curve at a chosen reference temperature. Fig. 5.a and 5.b display respectively the experimental compliance curves recorded at several temperatures between 25 and 57°C (for an applied stress level of 5 MPa), and the compliance mater-curve at the reference temperature of 25°C for *Adhesive 1*. From this master curve, it is then easy to determine the long-term evolution of the creep strain for the material under study, and to fit this curve with the Burger's model (Fig. 5.c.).

In the case of adhesive systems that exhibit a highly non-linear creep behavior, Houhou et al. (2014) have demonstrated that the previous TTSP procedure can be reproduced for various levels of applied stress, and one can finally identify a non-linear Burger's model. However, a drawback of the TTSP method is that the polymer adhesive is heated during the multiple isothermal tests, and this may affect its microstructure and provide unrepresentative results. This is especially true for cold-curing epoxies, which present usually an incomplete crosslinking after curing at ambient temperature.

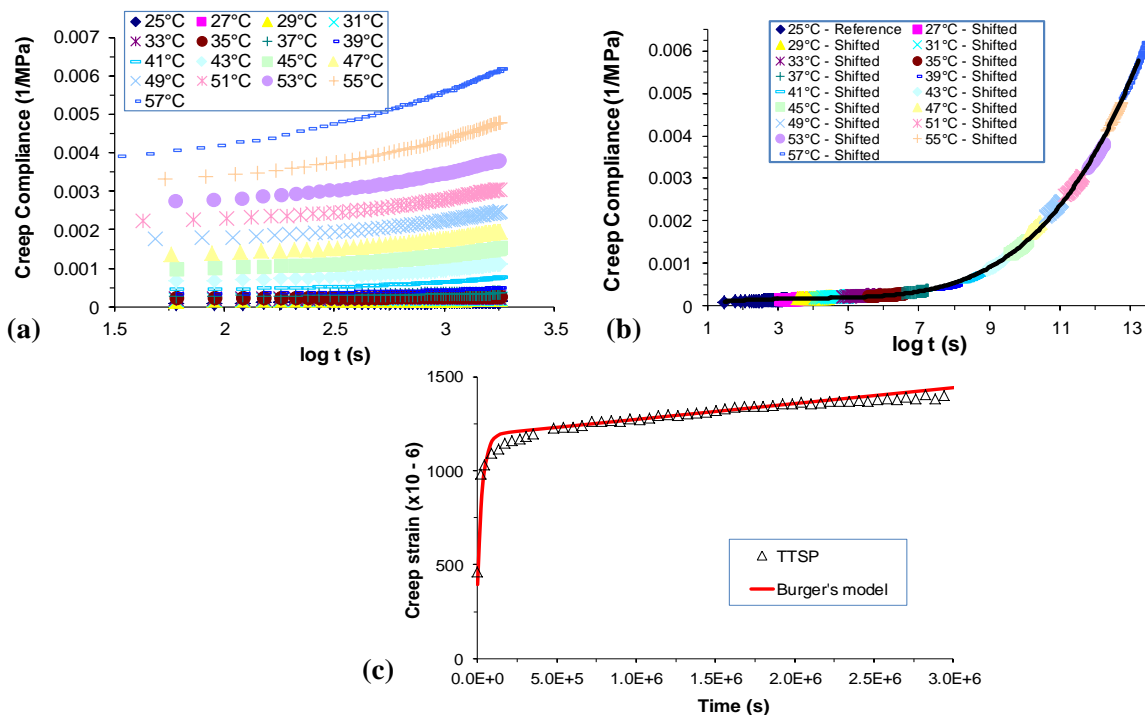


Fig. 5 - Creep compliance vs. time curves obtained from short-term creep tests under isothermal conditions for a stress of 5 MPa (a). Master curve for the reference temperature of 25 °C (b). Comparison of creep strain vs time curves obtained from TTSP approach and Burger's model (c)

An alternative predictive method based on the Time-Stress Superposition Principle (TSSP) might be more adapted for cold curing adhesive systems, as it doesn't require to heat the samples. It involves short term creep experiments at various loading levels, and the master-curve is again constructed by shifting the experimental compliance curves along the log-time scale axis. Fig 6. shows an example of application for *Adhesive 1*. Successive creep/recovery cycles (15 min creep/15 min recovery) were carried-out at several levels of applied stress in the range 3 - 25 MPa. Unfortunately, for the highest stress levels (above 20 MPa, which is lower than the expected tensile strength), a rapid failure of the samples was observed, due to the brittleness of *Adhesive 1*. For this reason, a master curve was built by shifting only the available creep compliance curves, providing a prediction of the creep behavior limited to 5 decades (10^5 s). Nevertheless, several authors have reported successful predictions up to $10^{7.5}$ s (one year) for other polymer materials (Jazouli et al, 2007), using this TSSP approach which remains of high interest.

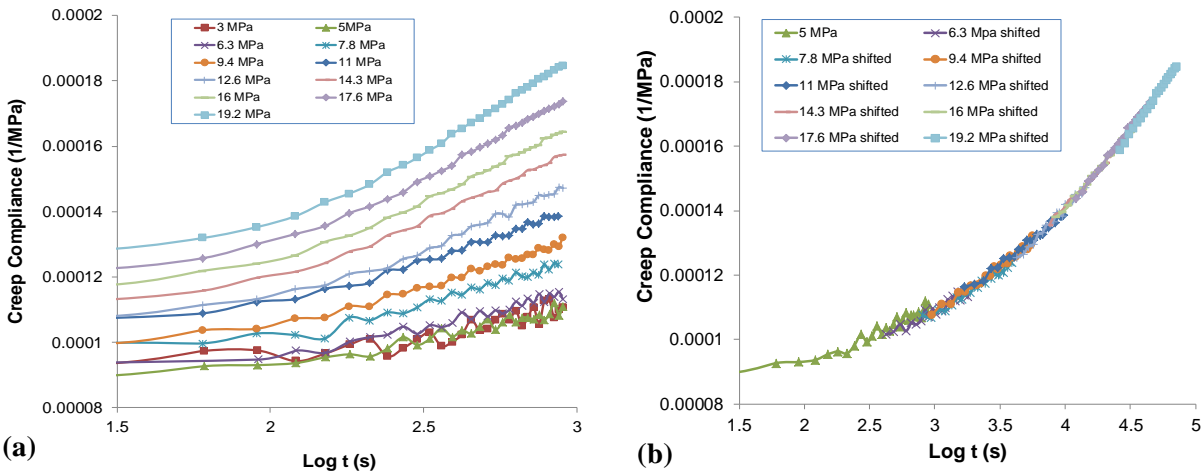


Fig. 6 - Creep compliance vs. time curves obtained from short-term creep tests at various load levels and at a temperature of 25°C (a). Master curve for a reference stress level of 5 MPa (b).

6. Conclusion

The present study has investigated the creep behavior of two selected cold curing epoxy adhesives, which are commercially available and commonly used in construction for the bonding of CFRP plates.

Preliminary physicochemical characterizations revealed significant differences in the composition and properties of the two systems, in terms of nature, content and size of the mineral fillers. Viscoelastic analyses performed on the unfilled matrices extracted from these two systems and cured at room temperature also demonstrated differences in terms of crosslink density of the epoxy networks.

Short-term tensile creep tests were then carried-out on cured samples of the two adhesives and their unfilled extracted matrices, showing that the level of the instantaneous elastic strain associated to the loading stage strongly depends on the filler content of the adhesive, while the creep rate depends upon both the molecular mobility of the epoxy network and the possible interactions between filler particles.

Finally, two predictive approaches were applied to evaluate the long-term creep behavior, based either on the Time-Temperature or the Time-Stress Superposition Principles. The first method appears to be very efficient but may provide unrepresentative results, as it requires heating the samples, which can alter their microstructure. The second method doesn't involve heating, but requires creep tests at high stress levels, which may be difficult, hence limiting the predictions to a few decades.

7. References

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