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Long-Term Development of Thermophysical and Mechanical Properties of Cold-Curing Structural Adhesives due to Post-Curing

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ABSTRACT: The long-term changes in the thermophysical and mechanical properties of a cold-curing structural epoxy adhesive were investigated by accelerating the curing reaction by post-curing at elevated temperatures. Experimental data concerning the glass transition temperature for periods of up to 7 years and tensile strength and stiffness measurements could be extrapolated for a period of up to 17 years. An existing model for the long-term development of concrete properties was modified for the prediction of the long-term mechanical properties of adhesives. The applicability of the acceleration procedure and the new model was confirmed by several verification procedures. Structural adhesives exhibit significant increases in glass transition temperature, strength and stiffness over the long term provided that joints are adequately sealed and protected from humidity and UV radiation. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: cold-curing structural adhesives; mechanical properties; epoxy resin; curing degree; glass transition temperature

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INTRODUCTION

Adhesive bonding is an effective connection technology already commonly used in the aerospace and automotive industries that is also starting to attract interest in the construction industry. Until now, however, adhesives were mostly used for nonstructural or semi-structural connections.[1,2] Structural applications are limited to certain cases where concrete bridge segments were bonded together or concrete bridge slabs were bonded to steel girders.[3,4] Another development is the strengthening of structures by bonding fiber-reinforced polymer composite laminates onto existing concrete or steel components.[5]

In the construction industry, connections have to be fabricated on the construction site and, due to time constraints, independently of the actual environmental conditions and season. Because of this, and the usually large size of the connections, the adhesives used in most cases are cold-curing thermosets. High-temperature curing or post-curing under controlled conditions as in industrial fabrication is normally not possible.

For adhesive bonding to be widely accepted in the construction industry, bonding during wintertime at comparatively low temperatures (5–10°C) must be possible. The early-stage mechanical properties strongly depend on the physical state of the adhesive when processes that take place during cure (such as gelation and vitrification) are governed by curing temperature and curing time.[6–9] However, low-temperature curing leads to an incompletely cured adhesive system as it greatly decelerates the development of full physical and mechanical properties, which can only be achieved after significantly longer curing periods or by post-curing. The increase in cure level and corresponding mechanical properties due to post-curing was discussed in Refs. 10–12.

The long-term behavior of structural adhesives is usually influenced by different factors, e.g., environmental parameters, such as temperature, humidity, and salinity, which lead to thermal and weathering ageing. These effects normally have a negative influence on the mechanical performance of the adhesive, leading to a reduction in mechanical properties. Furthermore, an increase in cure level with time leads to the formation of a more densely branched polymeric network that improves the mechanical behavior of adhesives.[12] This further increase in cure level is more evident in the case of well-sealed adhesive joints, where the effect of environmental conditions (such as humidity and salinity) can be much reduced or even eliminated. On the other hand, physical ageing of the adhesives might be relevant when the adhesive is exposed to temperatures below its glass transition temperature for long periods.[13] However, the physical ageing of cold-curing epoxy adhesives through different

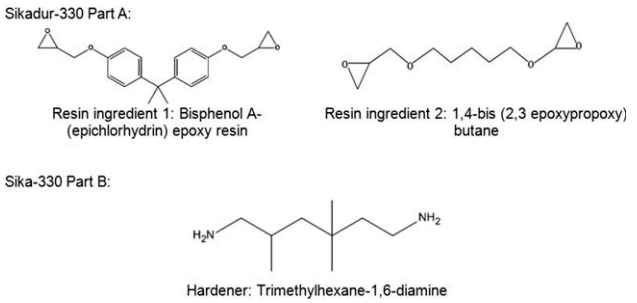

Figure 1. Chemical structure of resin and hardener.

exposure conditions up to 3 years was extensively studied by Frigione et al.[14] It was concluded that physical ageing has no significant effect on the T_g of the adhesive. Despite the extensive research performed, a model to predict the long-term development of the thermophysical and mechanical properties of cold-curing structural adhesives due to post-curing does not yet exist.

The long-term curing behavior of a cold-curing structural adhesive is investigated in this article. An accelerated experimental method based on post-curing of the adhesive at different temperatures is used to simulate the long-term improvement in physical and mechanical properties up to full cure. A model previously developed for predicting the long-term properties of concrete is modified to predict the long-term mechanical properties of cold-curing structural adhesives.

EXPERIMENTAL WORK

Material

The adhesive used was Sikadur-330 from Sika Schweiz AG, a thixotropic bi-component cold-curing epoxy adhesive, which is typical of epoxy adhesives used in structural applications. The chemical structure of the resin and the hardener are shown in Figure 1. The adhesive contains a small quantity of silica-based fillers (<20% by weight, based on burn-off investigation). Components are mixed at room temperature at a ratio of 4 : 1 by weight of the respective constituents (resin and hardener). The tensile strength and modulus of elasticity of specimens cured under laboratory conditions for 2 weeks and examined according to EN ISO 527-1 were 38.1 MPa and 4.6 GPa, respectively.[15] The glass transition temperature was 43.7 ± 0.7°C according to the Differential Scanning Calorimetry (DSC) investigation.

Experimental Set-up and Procedure

Thermophysical Experiments. A heat-flux differential scanning calorimeter (DSC-TA Q100) connected to a thermal analyzer was used to detect the heat released during the cure reaction. The DSC is equipped with a liquid nitrogen cooling system providing an inert atmosphere, thus allowing the DSC cell to reach low temperatures.

A total of 52 DSC samples, each weighing 5–10 mg, were examined. After curing under laboratory conditions for 2 weeks, post-curing at different temperatures and for different time periods was performed either outdoors, under laboratory conditions or in a climate chamber according to Tables I and II (further details are given in Section "Experimental Program"). Post-cured samples were then cooled under laboratory conditions during 24 h. The residual cure and the corresponding glass transition temperature, T_g, were obtained according to ASTM E 2602 by running a nonisothermal scan between −50 and 250°C at a heating rate of 5°C/min. Data acquisition was performed using the accompanying software (TA analysis).

Mechanical Experiments. A total of 55 tension specimens of Sikadur-330 were fabricated in aluminum molds (five specimens per mold) and examined according to ASTM D 638 as shown in Figure 2. Specimens were cured under laboratory conditions for 1 week. The post-curing of specimens was then carried out under different temperature and time conditions (as shown in Table II) and specimens were then cooled for 24 h at laboratory temperature.

Tensile experiments were performed using an MTS Landmark 25-kN servo-hydraulic load unit calibrated to 20% of its load capacity. Longitudinal strains were measured using an MTS clip-on extensometer mounted across the specimen as shown in Figure 2(b). The extensometer had a gage length of 25 ± 0.05mm and a minimum accuracy of ±0.5% of the measured strain. Experiments were performed under displacement control at a loading rate of 5 mm/min. Five specimens were examined for each condition and the results obtained for a minimum of three specimens were analyzed after discarding specimens with flaws or voids and specimens exhibiting a tab failure.

Experimental Program

To investigate the long-term change in T_g, DSC samples were prepared from adhesive material cured under laboratory conditions (T = 23 ± 5°C and RH = 50 ± 10%) for different time periods, t, of between one and 7 years, as shown in Table I. Similar samples were prepared from material exposed to outdoor curing (in Lausanne) between 2003 and 2010 for comparison of results with samples cured at laboratory temperature. A minimum number of two samples were examined for each curing condition.

Furthermore, several sets of tensile specimens and DSC samples were examined. The long-term development was simulated by accelerating the reactions by post-curing at elevated temperatures. The tensile specimens and DSC samples from one set, denominated the reference set, were examined immediately after curing (no post-curing involved). The obtained strength and stiffness values and the corresponding glass transition temperature, T_g, were used as reference values during the analysis in

Table I. Experimental Program for DSC Samples Cured During Several Years

Curing Condition	Laboratory					Outdoors		
t (yr)	1	2	3	4	5	6.75	6.75	7.25
Physical								

Table II. Experimental Programs for Post-curing of DSC Samples and Tensile Speimens

	Procedure			Verification (1)			Verification (2)			Verification (3)	
T_{pc}(°C)	Reference			60°C			40°C			~ 23°C	
t_{pc}	0	4	8	24	72	168	24	48	168	2160	17520
Physical											
Mechanical											

order to observe the changes in properties after subjecting the material to various post-curing conditions. Post-curing of several sets was then performed in the climate chamber under different conditions as shown in Table II. Four experimental groups can be characterized as follows:

Group 1, designated as the procedure group in Table II, consists of the reference set in addition to two sets of tensile specimens and DSC samples post-cured at 60°C during 4 and 8 h to establish the model. Group 2, designated as verification 1, consists of three sets of tensile specimens and DSC samples post-cured at 60°C during 24, 72, and 168 h. Results from this group are used to verify the applicability of the model when extrapolated. Group 3, designated as verification 2, consists of three sets of tensile specimens and DSC samples post-cured at 40°C during 24, 48 and 168 h. Results from this group are used to investigate the effect of post-curing temperatures below T_g. Group 4, designated as verification 3, consists of two sets of tensile specimens cured under laboratory conditions only (~ 23°C) during 3 months and 2 years. Results from this group are used to verify the applicability of the experimental method (accelerated curing procedure) and further verify the developed model.

Moreover, additional verification of the ultimate T_g of the adhesive was carried out by post-curing DSC samples at 100°C during 24 and 72 h.

EXPERIMENTAL RESULTS AND DISCUSSION

Thermophysical Behavior

The change in T_g over a long-term period of up to 7 years is shown in Figure 3. An almost bi-linear increase in T_g took place. After 1 year, T_g increased by ~ 29% while the increase after 7 years was 42%. An increase in T_g may occur due to the continuation of cure and/or physical ageing of the adhesive. The latter was detected by enthalpy relaxation peaks in the DSC scans of some samples; details are presented in Ref. 16. This result agrees with results reported in Ref. 14 for a similar structural cold-curing adhesive. It was found, however, that on the long-term (up to 3 years) and for different exposure conditions, there is no effect of physical ageing on the T_g. Physical ageing had an effect only when combined with chemical ageing. Samples cured outdoors showed an additional increase in T_g due to their exposure to higher temperatures (>30°C during certain

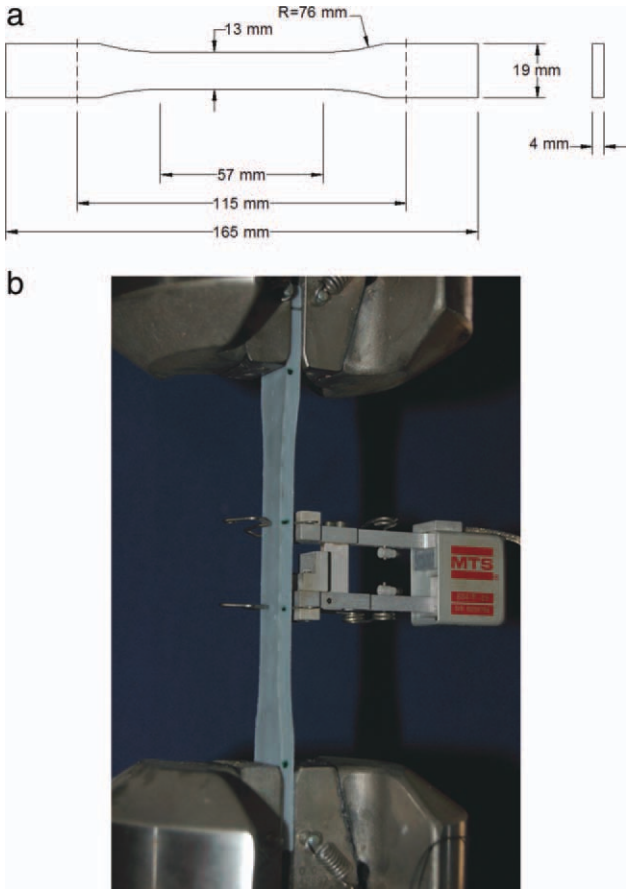

Figure 2. (a) Specimen dimensions according to ASTM-D638 and (b) Experimental set-up. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

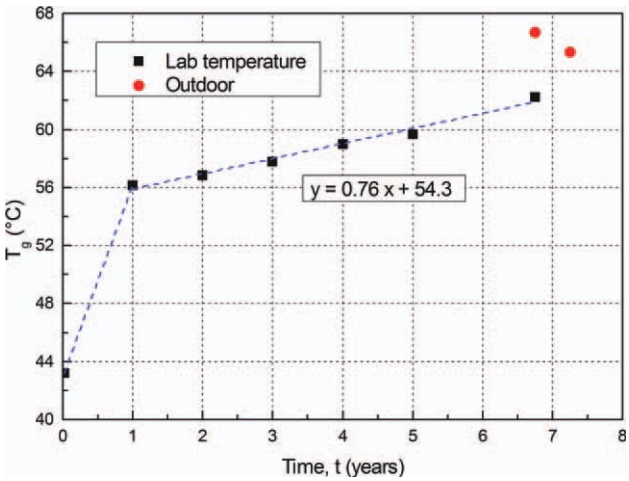

Figure 3. Measured T_g versus time for samples cured for up to 7 years. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

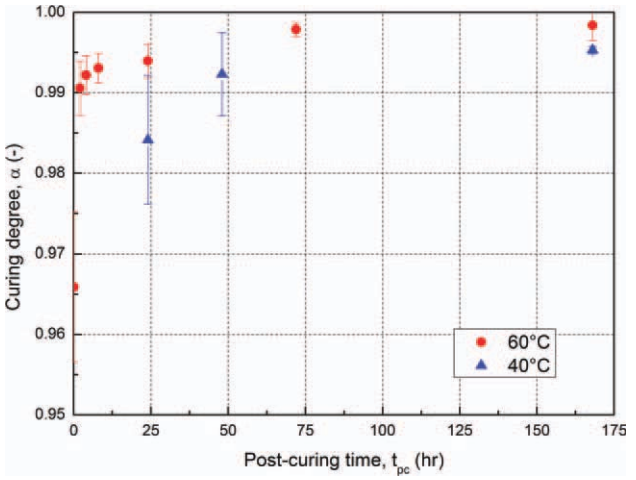

Figure 4. Curing degree versus time for samples post-cured under different conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

summers) compared to samples cured in the laboratory. It was not possible to measure exactly the small changes in curing degree corresponding to these high T_g values due to the difficulty in precisely monitoring the insignificant residual cure that took place during the later stages of the curing process. However, it could be concluded that a curing degree exceeding 98% was achieved by all samples (see Ref. 16 for experimental details and raw data).

The development of curing degree, α, and T_g versus post-curing time, t_{pc}, is shown in Figures 4 and 5 for the post-curing of samples at 40 and 60°C (results from all experimental sets are given). The curing degree increased from an average of 96.5% (reference set cured for 2 weeks under laboratory conditions) to above 98 and 99% for samples post-cured at 40 and 60°C, respectively. This increase was attributed to the increase in thermal energy supplied to the system, leading to an acceleration of curing reactions and resulting in a higher degree of cross-linking (that of reactive groups that react very slowly at low-curing temperatures such as secondary amino groups or sterical hindered amino groups was particularly accelerated). Despite the small increase in curing degree, a significant increase in T_g of around 41 and 63% was observed when samples were post-cured for 1 week at 40 and 60°C, respectively.

The maximum attainable T_g (73°C ± 1.3, denominated ultimate T_g in Section "Experimental Program") was obtained by post-curing samples at 100°C for 72 h, as shown in Figure 5. Similar results were achieved at 60°C for 168 h. Therefore, the maximum attainable T_g of the adhesive can be assumed as being ~ 73°C.

By approaching the almost bi-linear increase of T_g with time, as shown in Figure 3, using a logarithmic fitting up to the ultimate T_g, the equivalent time, t_{eq}, required to achieve the same T_g values when the adhesive is cured under laboratory conditions was determined, as shown in Figure 6. A relationship between the post-curing time and equivalent curing time required at laboratory temperature is then obtained, as shown in Figure 7. A dependence on the post-curing temperature was observed. The rate of increase in T_g was higher when the post-curing temperature was increased above T_g (at 60°C). Post-curing below T_g (at 40°C) also resulted in an increase in T_g but at a lower rate. For instance, a post-curing time of 72 h at 60°C would result in a T_g equivalent to that obtained during 14.8 years at laboratory temperature or almost 2 years at 40°C.

Mechanical Behavior

The development of tensile strength and stiffness for specimens post-cured at 60 and 40°C is shown in Figures 8(a,b), respectively. By knowing the corresponding T_g, the equivalent time required to achieve a certain property level under laboratory conditions was derived from Figure 6. An increase of 48 and 15% was attained for tensile strength and stiffness respectively by post-curing at 60°C for 1 week (168 h), which is equivalent to ~ 17 years.

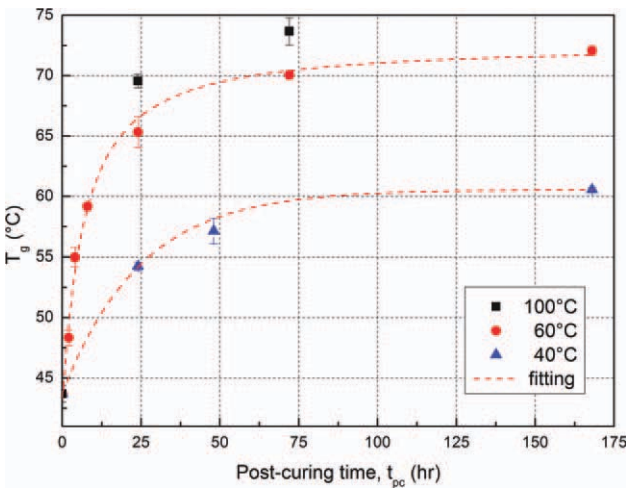

Figure 5. T_g versus post-curing time for samples post-cured at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

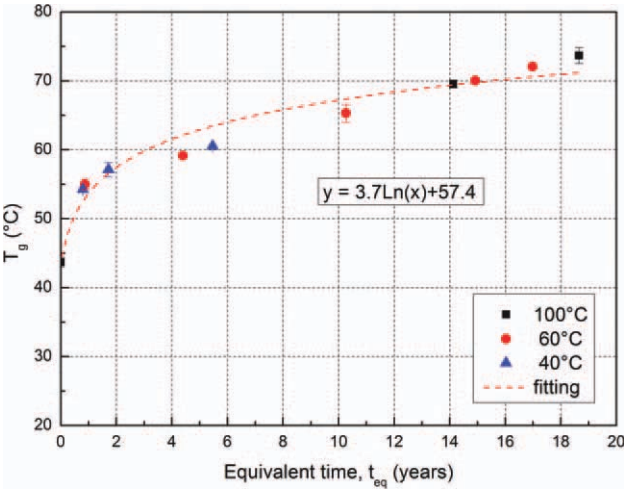

Figure 6. T_g versus equivalent time under laboratory conditions for samples post-cured under different conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

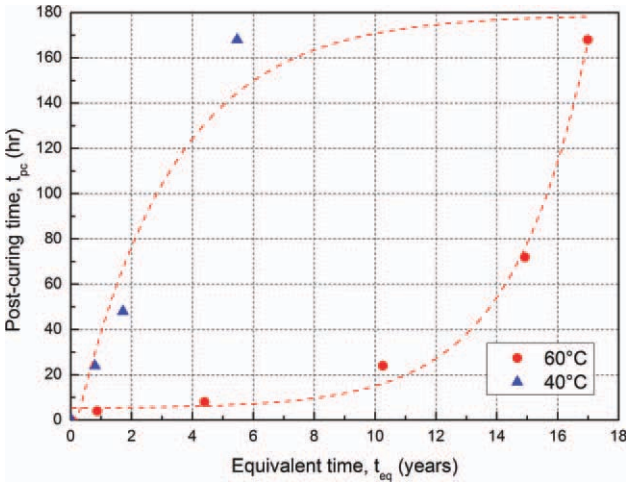

Figure 7. Time required for curing of samples at laboratory temperature compared to postcured samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Tensile strength increased more significantly than stiffness for two possible reasons: firstly, strength is more dependent on changes in the polymeric structure regarding an increase in chain branching and molecular bond strength, which is also demonstrated by the increase of strain at failure after post-curing, as shown in Figure 9. In addition, the fillers contained in the material contribute more to the stiffness than the strength and therefore the change in stiffness due to changes in the polymeric structure is smaller than the change in strength. An increase in mechanical property values for specimens post-cured at 40°C (verification 2) was also observed albeit at a slower rate than those post-cured at 60°C during the same periods (verification 1). Specimens cured at laboratory temperature for longer periods (verification 3) were found to follow the same trend. Of all the experimental groups, the results of group 2 specimens (verification 1) showed the biggest scatter, which could be attributed to an insufficiently long cooling period (24 h).

The relationship between tensile strength and stiffness is shown in Figure 10. The quasi-linear relationship between these properties found during curing at early age by Moussa et al.[7] was not confirmed at high curing degrees. A deviation in the long-term relationship between tensile strength and stiffness was observed, which can be attributed to the more significant increase in strength than stiffness.

MODELING AND DISCUSSION

Existing Models for Concrete Curing

The curing behavior of both structural adhesives and concrete (setting of cement) is characterized by an exothermic reaction. The mechanical properties of both materials at young age are dependent on the curing reaction, and an increase in mechanical properties occurs over the long term.[7,17–19] Therefore, a model presented for concrete is adopted to predict the long-term development of adhesive properties.[20] The concrete model assumes that the rate at which concrete compressive strength increases with time depends on a variety of parameters, in particular, the type and strength class of the cement, type and amount of admixtures and additions, water/cement ratio and environmental conditions. The development of compressive strength with time is estimated as follows:[20]

$$f_{cm}(t) = \beta_{cc}(t) f_{cm} \tag{1}$$

with

$$\beta_{cc}(t) = \exp\left\{ s\left[1 - \frac{28}{t}\right]^{0.5} \right\} \tag{2}$$

where $f_{cm}(t)$ is the mean compressive strength at a concrete age of t in days, f_{cm} is the mean compressive strength at a concrete age of 28 days, $\beta_{cc}(t)$ is a function describing the development of compressive strength with time, t is the concrete age in days and s is a coefficient which depends on the strength class of the cement. These equations are valid for a concrete temperature of 20°C. For temperatures other than 20°C, a temperature-adjusted concrete age should be used.

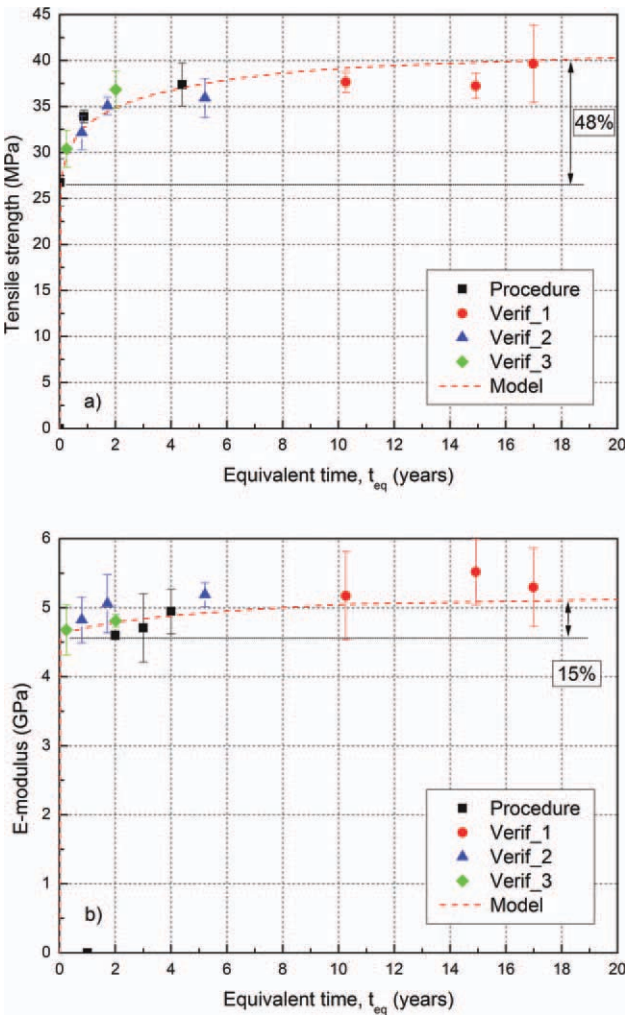

Figure 8. Mechanical property development due to post-curing for predicting long-term material behavior—(a) strength and (b) stiffness. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

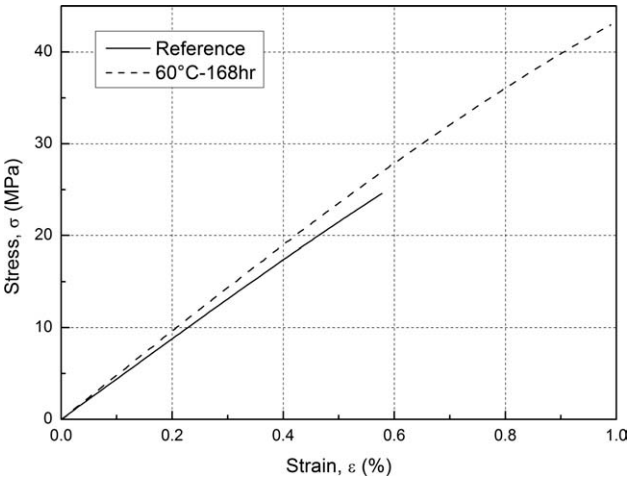

Figure 9. Change in stress–strain behavior of selected specimens due to post-curing.

The development of the tensile strength of concrete with time is much more difficult to predict because it is significantly influenced by the development of shrinkage stresses, which in turn depend on structural member size and curing conditions. Therefore, in the case of a concrete age exceeding 28 days, it may be assumed that the development of tensile strength with time is similar to that of concrete compressive strength.[20]

The modulus of elasticity of concrete develops more rapidly than compressive strength. $E_c(t)$ is to a large extent influenced by the modulus of elasticity of the aggregates, which in turn is independent on concrete age. This is taken into account in the following equations:

$$E_{ci}(t) = \beta_E(t) E_{ci} \tag{3}$$

with

$$\beta_E(t) = [\beta_{cc}(t)]^{0.5} \tag{4}$$

where $E_{ci}(t)$ is the tangent modulus of elasticity at a concrete age of t in days, E_{ci} is the tangent modulus of elasticity at a concrete age of 28 days, and $\beta_E(t)$ is a function that describes the development of the modulus of elasticity with time.

New Model for Cold-Curing Adhesives

The model developed for concrete compressive strength development was adopted to predict the long-term change in the strength and stiffness of structural adhesives as follows:

$$P(t) = \beta_P(t) P_7 \tag{5}$$

where P_7 is the value of the mechanical property after seven days' curing under laboratory conditions as usually given in the datasheets provided by most manufacturers of commercial adhesives. Assuming that the mechanical properties are governed by the physical state of the adhesive, the s factor in eq. (2) was replaced by the term, $\beta_p(t)$, expressing the change in T_g with time as follows:

$$\beta_P(t) = \exp\left\{ \left(1 - \frac{7}{t}\right)^{0.5} \left[\frac{T_g(t) - T_{g,7}}{T_{g,7}}\right]^n \right\} \tag{6}$$

where $T_g(t)$ is the glass transition temperature of the adhesive at time t determined as the midpoint of the T_g step in DSC curve (used in this work) or as the peak point of the tan δ curve during DMA, $T_g(7)$ is the glass transition temperature of the adhesive after 7 days' curing at 23°C (laboratory conditions) and n is a property-dependent parameter describing long-term property development. Because of the negligible influence of shrinkage during the curing of adhesives, the compressive and tensile strengths can be described by the same model. Stiffness can also be described using the same model as applied for concrete stiffness in eq. (3). Moreover, the development of adhesive strength and stiffness are similar regardless of the rate of development, as demonstrated in Ref. 7.

Modeling Results

The values of n for tensile strength and stiffness were obtained by fitting eq. (6) to the experimental results (the procedure

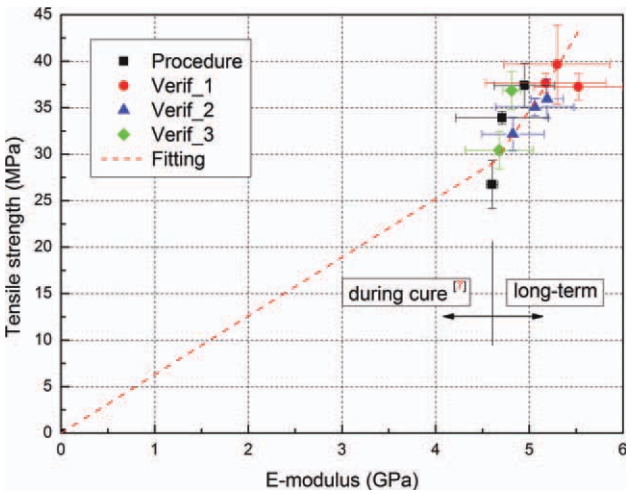

Figure 10. Tensile strength versus stiffness relationship. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

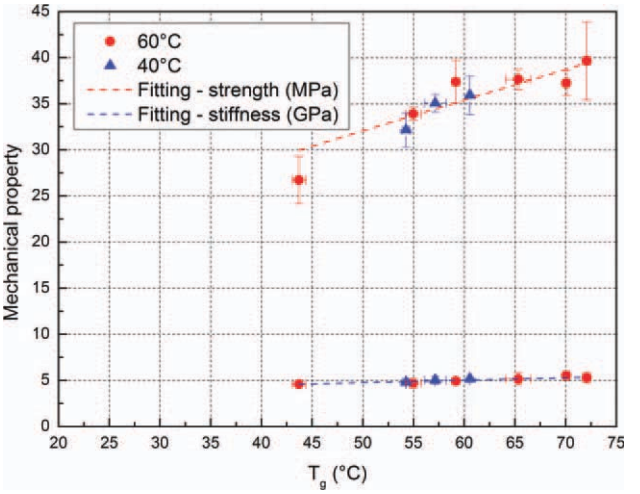

Figure 11. Change in strength and stiffness versus T_g after post-curing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

points in Table II) and applying the corresponding T_g values shown in Figure 8. Values of 1.06 and 2.62 for tensile strength and stiffness were obtained, respectively. The value of n resulting from the fitting of strength results (~ 1) indicated that the rate of change in strength and T_g is somewhat similar; on the other hand the rate of change in stiffness was lower than that of T_g and consequently strength, yielding to an n value > 1. The rate of change of mechanical properties with respect to T_g is also confirmed by the experimental results, as shown in Figure 11. A steeper slope was obtained in the case of strength, agree with the results shown in Ref. 7, confirming that stiffness approaches the maximum value during the short term curing while longer time periods are necessary for achieving maximum strength.

Three sets of verifications were performed as previously mentioned. First, the model was extrapolated (using the same n values obtained from the fitting) and the modeling curve was compared to results for specimens post-cured at 60°C for longer periods (verification 1). A good agreement was found. Moreover, the results for specimens post-cured at 40°C (verification 2) compared well to the modeling curve and therefore confirmed the possibility of post-curing at temperatures below T_g, regardless of the rate of increase in properties. The third verification was performed using specimens cured under laboratory conditions for long periods (verification 3). The model also compared well to these experimental results, therefore confirming the applicability of the accelerated curing method and the validity of the model.

According to the new model, the values of tensile strength and stiffness after 50 years (an average bridge service life) would be 44.0 MPa and 5.5 GPa respectively. These values show an increase of 11 and 3%, respectively compared to the maximum experimental results achieved (equivalent to $\sim$ 17 years of ambient curing).

CONCLUSIONS

The long-term changes in thermophysical and mechanical properties of a cold-curing structural adhesive were investigated by accelerating the curing reaction by post-curing at different temperatures above and below T_g during different periods. Only temperature effects are taken into account; other aggressive environmental agents, e.g., humidity and salinity, can further affect the long-term behavior of the adhesive. A new model was established to predict the change in the mechanical properties of structural adhesives by taking into account the change in the adhesive's physical state. The following conclusions were drawn:

- The experimental data available concerning the glass transition temperature, T_g, for periods of up to 7 years could be extrapolated for a period of up to 17 years by accelerating the curing reaction by post-curing at elevated temperatures (slightly above and below T_g).
- Based on this extrapolation procedure, tensile strength and stiffness measurements could also be extrapolated for up to 17 years.
- An existing model for the long-term development of concrete properties was modified for the prediction of the long-term mechanical properties of adhesives. The applicability of the acceleration procedure and the new model was confirmed by several verification procedures.
- Structural adhesives exhibit significant increases in T_g, strength and stiffness over the long term provided that joints are adequately sealed and protected from environmental impact, particularly humidity and UV radiation.

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