Fourth International Conference on FRP Composites in Civil Engineering (CICE2008)
22-24July 2008, Zurich, Switzerland

CURING BEHAVIOUR OF EPOXY-ADHESIVES FOR BONDED CFRP-REINFORCEMENTS

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ABSTRACT: Polymers open access to new production methods. This also applies for civil engineering. Post-strengthening of concrete structures with bonded CFRP-straps is only one example. For the successful application of such a method the specific mechanical behaviour of the polymers used, especially their temperature and time dependency needs to be considered. Curing of the adhesives that are used is usually determined by stamp pull-off tests. By this method only the adhesion between material and concrete is examined. Thus, the cohesion of the material which dominates the long-term behaviour and the mechanical properties of the material itself are not taken into account. These properties are strongly influenced by the degree of cure of the adhesive. In the scope of this paper a commercial cold curing epoxy based adhesive for bonded CFRP-reinforcements was investigated by means of thermal analysis and mechanical testing. The development of the degree of cure and glass transition temperature (T_g) was determined for curing at room and minimum allowable processing temperature. It was correlated to mechanical short and long-term properties. In addition to that the thermal application limits of the material were determined by dynamic mechanic analysis (DMA).

1 INTRODUCTION

During the lifespan of a building requirements for the structure may change, e.g. by an additional load, decay of the building material, or damages of the framework as a result of an accident or fire. Hence in the 1970s a technique for post-strengthening concrete structures by externally bonded reinforcements was developed. In the beginning steel straps were used while in the recent past predominantly CFRP-straps made of a unidirectional carbon fibre reinforcement and an epoxy resin matrix are bonded either to the surface of the concrete or into prefabricated slits (Regnault 2000, Meier 2000, Blaschko 2001).

In order to ensure a successful application of the polymers the environmental conditions during processing and application need to be considered. In case of bridges this can be the temperature and influences by alkaline media. Long-term measurements at a bridge of the Inntal-motorway show that even below the tarmac, where bonded CFRP-reinforcements can be installed in order to reinforce the bridge's cantilever beam, temperatures can rise up 53 °C during summertime (Lötsch et. al. 1976, Zilch et. al. 2004). That means that the knowledge of the thermal application limit and creep behaviour of the reinforcement system consisting of a CFRP-strap and the adhesive is of great importance. Both are directly related to the degree of cure reached by the adhesive.

In the scope of this paper the curing behaviour and the correlating mechanical properties of a commercial adhesive is determined by means of thermal and mechanical analysis. Systematics for the determination of thermal application limits by means of dynamic mechanical analysis (DMA) is presented.

2 THEORETICAL BASICS

2.1 *Thermal application limits*

Using polymers as constructive material their special viscoelastic deformation behaviour and above all the strong temperature dependency of the mechanical properties need to be considered. Initially the modulus of elasticity continuously decreases with rising temperatures. Due to an over proportionally increasing movability of the molecules, mechanical properties change dramatically at the change-over from the glassy (energy-elastic) to the rubbery (entropy-elastic) state. This softening region is called the glass-transition region and can easily spread over some 20-30 °C for thermosets such as epoxy adhesives used for bonded CFRP-reinforcements. The center of the glass-transition region is usually referred to as the so called glass-transition temperature (T_g). That means that the material starts softening several degrees below T_g and can lead to a drop in the modulus of elasticity of up to 3 decades. Thus an application of such a material beyond the softening point can be critical and defining T_g as an application limit appears to be inappropriate (Hülder et. al. 2006).

Two major aspect have to be taken into account. On the one hand the deformation behaviour of polymers divides into three deformation classifications which are elastic, relaxating, and viscous. The glass-transition temperature is usually determined for very small strains, so that almost only elastic deformation occurs which shows the least dependence on time, load level, and temperature. Thus the determined values for T_g will represent a maximum. On the other hand the softening region and the glass-transition-temperature respectively will shift to higher temperatures as the adhesive cures. The degree of cure is influenced by the environmental conditions while curing, so that even cold-curing adhesives may not fully cure under building site conditions.

A useful systematic for the determination of a thermal application limit by means of dynamic mechanical analysis (DMA) which is presented in DIN 65583 and was originally developed for the determination of application limits of FRP-materials used in aircraft constructions. It suggests that the application limit is represented by a 2 % drop of the modulus compared to the continuous descent of the modulus' well below T_g, figure 1. This allows determining an application limit which guarantees a sufficient offset to T_g.

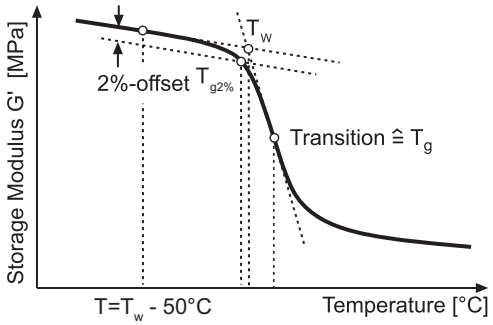


Figure 1. Begin of the glass-transition region according DIN 65583
$T_{g2\%}$ Begin of softening according to the 2%-Method
T_w Begin of the glass-transition region according to the tangent method
T_g glass-transition-temperature

2.2 *Curing of thermosets*

In contrast to thermoplastic materials thermosets polymerise during the manufacturing process. That means that during the curing process of a material the reactive groups of the resin's and hardener's monomers will combine and form a three dimensional network. Hence the material properties change with the generated network and the so called degree of cure.

The degree of cure corresponds to the ratio of generated covalent bonds during the reaction and of the total number of potential covalent bonds that will be generated if the resin is fully cured. Thus with an increase of the degree of cure the network density rises which consequently

leads to an increase in the mechanical properties such as stiffness, rigidity and creep behaviour as well as chemical and aging resistance and T_g.

As the number of reactive groups can not be directly quantified the degree of cure is usally determined by means of thermal analysis such as the differential scanning calorimetry (DSC) which allows to measures the specific reaction enthalpy which is represented by change in the specific heat flow as a result of exothermal reactions. The ratio of the specific residual enthalpy Δh_{res} of a cured sample and the total specific reaction enthalpy Δh_{tot} of an uncured sample, both of which are determined in dynamic DSC runs is defined as the degree of cure (c_{DSC}) (Ehrenstein et. al. 1998):

$$c_{DSC} = \left(1 - \frac{\Delta h_{res}}{\Delta h_{tot}}\right) \cdot 100\ [\%] \tag{1}$$

Especially for slowly curing resins the residual enthalpy may be rather small and hard to measure. Reaction processes that cannot be detected by the residual enthalpy often lead to a significant alteration in the glass transition temperature (T_g) and network density, as at the end of the curing reaction complete parts of the network get constricted in their mobility by only a few chemical bonds. Thus T_g is a direct measure for segment mobility in amorphous polymers, and reacts more sensitive, so that even very high degrees of curing can be distinguished (Ehrenstein 2006)

3 PERFORMED TESTS

3.1 *Investigated material*

In the presented work a commercial cold curing epoxy adhesive for externally bonded reinforcements was investigated according to its curing, thermomechanical and creep behaviour. The adhesive consists of approx. 25 % of epoxy resin filled with 10 % of chalk and 65 % of other anorganic fillers (predominantly SiO_2). The adhesive is approved for bonded reinforcements in combination with pultruded CFRP-straps on the concrete's surface as well as in prefabricated slits. The material may be processed at temperatures between 8° C and 40 °C. The maximum application temperature is stated with 45 °C.

For the mechanical investigation test specimens type A according to DIN EN ISO 527 were produced by mixing the resin and hardener in accordance to the manufacturer's instructions and carefully filling the mixture into special PTFE-forms. Curing took place at a constant temperature of 8 °C which is the minimum processing temperature for the adhesive and 23 °C for curing times differing between 48 h and 28 days

3.2 *Differential scanning calorimetry (DSC)*

For the different curing times and temperatures the degree of cure and glass transition temperature was determined by dynamic DSC-measurements (TA Instruments Q1000; heating rate 20 K/min, sample mass approx. 20 mg). Samples were taken directly from the tensile test specimens, so that the degree of cure could be directly correlated to mechanical properties.

3.3 *Mechanical Testing*

Tensile tests were performed according to DIN EN ISO 527 with an electro-mechanical tensile testing machine (Zwick 1484). In order to analyse the mechanical behaviour at minimum (8 °C) and room temperature as well as elevated temperatures (40 °C, 50 °C, and 60 °C).

For the dynamic tests a heavy duty DMA (Gabo Eplexor 500) was used which allows dynamic loadings up to 500 N. Therefore, it is possible to reach the non-linear viscoelastic range so that the mechanical behaviour can be examined under conditions that are closer to real life applications. The sample dimensions were 2 x 4 mm with a clamp distance of 40 mm. Testing

was performed with a heating rate of 3 K/min and a measurement frequency of 3 Hz. The samples were cut from the same type of specimens that were used for tensile testing.

In order to regard the variable material behaviour at different loading levels dynamic tests were realised at two different loading levels (0,01 % to 0,04 % for low and 0,03 % to 0,17 % strain for higher load levels). The thermal application limits were derived from these measurements as described above according to DIN 65 583. In addition to that the heat deflection temperature (HDT) according to ISO 75-1/2 method A was also determined.

Creep tests were performed according to DIN 53444, using tensile testing specimens that were cured for 48 h at 23 °C. The test were accomplished over a period of 1000h at 23 °C at 50 % atmospheric moisture with a constant load of 6 N/mm² which comes up to 20 % of the tensile strength.

4 EXPERIMENTAL RESULTS

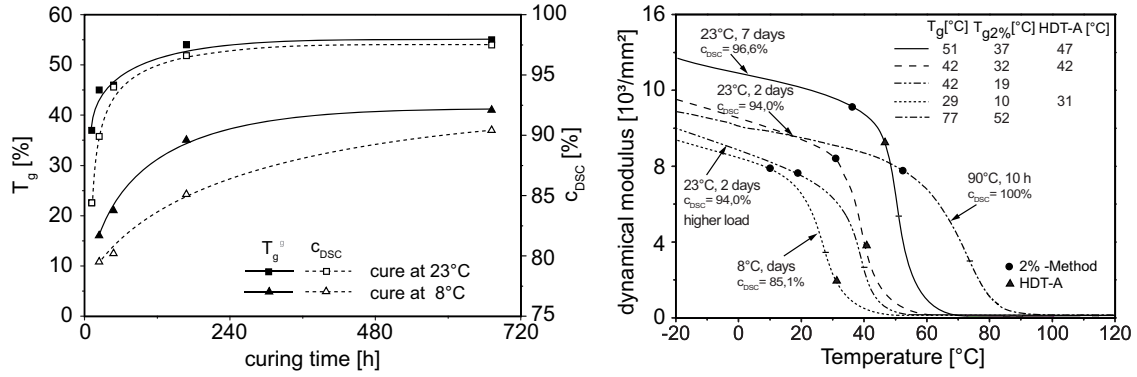
4.1 *Differential scanning calorimetry (DSC)*

The degree of cure determined by DSC shows a strong dependency on time and temperature, as the mobility of the molecules rises with the temperature and the reaction accelerates.

Figure 2a shows the development of T_g and c_{DSC} for different curing times and temperatures. Increasing curing times lead to a rise in T_g. It rises from 46 °C after 48 h to 54 °C after 7 days of curing. With a higher density of the macromolecular network the reaction process slows down, as the reaction kinetics get predominantly diffusion controlled. Thus only 1 °C is added to T_g after 28 days. After that no further significant change in T_g is to be expected. Therefore it is advisable to prolong the support time before loading the construction from 48h as stated in the technical approval to at least one week. For the minimum allowable processing temperature of 8 °C the progression of T_g shows an even slower increase so that only 41 °C are reached even after 4 weeks. Hence it has just reached the level of a sample cured at 23 °C for only 12 h.

DMA measurements at low loading levels represent the typical run of the elastic modulus curves, figure 2b. An increase in curing time at 23 °C from 48 h to 7 days leads to an increase of T_g from 42 °C to 51 °C. Thus the thermal application limit derived using the 2 %-method rises from 32 °C to 37 °C. However higher loading levels that are closer to real life applications lead to lower initial stiffness, and to a lower $T_{g2\%}$, although T_g is the same for low and elevated load levels. For a curing temperature of 8 °C T_g does not exceed 29 °C even after 7 days of curing. A sample cured at 90 °C for 10 h to ensure a maximum degree of cure has a glass transition temperature of 77 °C and Tg2% lies at 55 °C and thus almost 25 °C above the thermal application limits reached for curing at room temperature.

Determining the HDT according to EN ISO 75 leads to higher thermal application limits than the ones derived with the 2 %-method. When plotted into the DMA-curves HDT values lie very close to T_g. Thus this method appears to be inappropriate for the determination of the thermal application limits, as it overestimates the potential of the material.



a) b)

Figure 2a: development of T_g and c_{DSC} in dependence of time and temperature
Figure 2b: influence of the degree of cure on the adhesives thermal application limits

4.2 *Mechanical Testing*

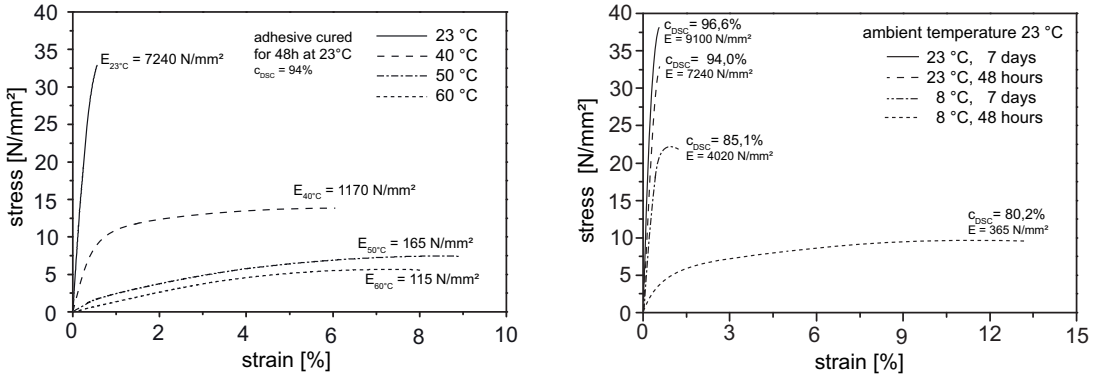


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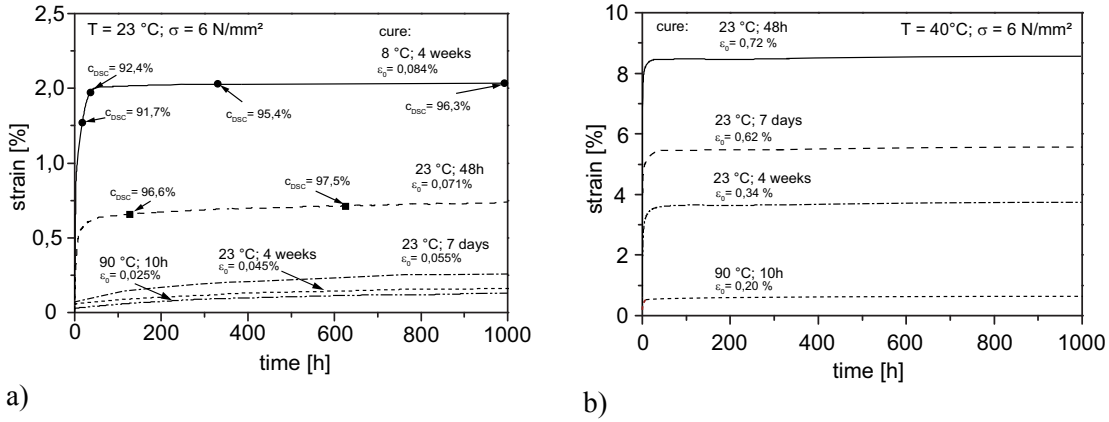
Figure 3a: stress-strain curve for different degrees of cure (ambient temperature 23 °C)
Figure 3b: influence of the degree of cure on the adhesives thermal application limits

Mechanical tests support the results derived from DMA. For a sample cured at 23 °C for 48 h the tensile strength for an ambient temperature of 23 °C lies at 32 N/mm² and shows a rather brittle material behaviour. Testing at 40 °C, which lies 8 °C over $T_{g2\%}$, but still below T_g however leads to a significant reduction of tensile strength (14 N/mm²) and stiffness. At 60 °C the tensile strength even drops to 6 N/mm². Thus it appears not possible to ensure a sufficient transfer of stresses from the concrete to the CFRP-straps above the presented application limit.

Figure 3b shows the tensile strength in dependence of the curing time and temperature at a testing temperature of 23 °C. Even after a curing time of 7 days at a curing temperature 8 °C the tensile strength and stiffness only reaches approximately 60 % of the values for curing at 23 °C for 48 h. The increase of the degree of cure as a result of curing time and temperature clearly correlates with the alteration of mechanical properties, such as rigidity and stiffness.

Not only short-term material properties show a strong dependency on the degree of cure but also the long-term properties such as the creep tendency. Figure 4a shows the creep curves of the adhesive at room temperature. In compliance with the results of the tensile tests and DMA a strong dependency on the curing time and temperature can be found. Samples with a comparatively low degree cure such as samples cured for 4 weeks at 8 °C or samples cured for 48 h at 23 °C show a significant, over proportional increase in creep strain within the first 3 days. For the samples cured at 8 °C for 4 weeks this strain is almost 4 times as high as for samples cured for 48 h at 23 °C. The curves of both samples show a rather sharp bend after 75 h, since the degree of cure rises due to post-cure during the creep tests.



a) b)

Figure 4a: creep curves of the adhesive in dependence on the curing conditions (ambient temp. 23 °C)
Figure 4b: creep curves of the adhesive in dependence on the curing conditions (ambient temp. 40 °C)

In contrast to that samples were only little post-cure has to be expected show a much flatter creep curve. The maximum creep deformations differ by almost 800 % between a fully cured sample and samples with an initial degree of cure of approximately 90 % (curing at 8 °C for 4 weeks).

When the testing temperature exceeds the thermal application limits that were determined according to the 2 %-method, creep strains rise to a multiple of the values measured at room temperature. In case of samples cured at 23 °C for 48 h the over all creep strain is more than 10 times higher than at room temperature. For all three samples a sharp bend can be seen after approximately 24 h. After that the slope of the creep curves becomes rather flat and the curves run almost parallel to the curve of a fully cured sample. In compliance with the tests performed at 23 °C this bends correlates with post-cure effects.

Thus an increase in temperature close to the current T_g leads to an increase in the molecular movability that leads to high creep deformations at the beginning while it also restarts the curing reaction which leads to an increase in the degree of cure and T_g respectively. As a consequence the creep tendency reduces after a while.

5 CONCLUSION

For the evaluation of thermal application limits of bonded reinforcements of concrete framework parts the knowledge about the adhesive's curing behaviour and the lowering of mechanical properties under temperature influence is of particular importance. Defining the glass transition temperature as application limit is not reasonable, as the softening of the material already starts at lower temperatures. It is suggested to determine application limits according to DIN 65583. Furthermore it needs to be considered, that this limit will move towards lower temperatures with increased loading levels.

DSC-measurement allows determining the reaction kinetics of an adhesive. Thus it is suggested that for future technical approval not only stamp pull-off test but also tests concerning the reactivity of the material should be performed. Once they are determined it is possible to predict the degree of cure that will be achieved under certain conditions.

Finally it should be borne in mind that bonding takes place under building site conditions, so that even lower degrees of cure and thus lower application limits must be expected than the ones derived under laboratory conditions and stated in this paper. Hence a continuous monitoring of the adhesive directly at the building would be desirable.

As it appears to be unpractical to monitor bonded reinforcements on the building by means of DSC other methods need to be developed. One promising method could be measuring the dielectric properties of the adhesive as they correlate with the network density and the degree of cure respectively.

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