MECHANICAL BEHAVIOUR OF EPOXY NETWORKS IN DEPENDENCE ON TIME, CURE AND TEMPERATURE

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Abstract

Thermoset polymers like epoxy networks provide excellent mechanical and thermal properties and are widely known for their use as matrix material for high performance composites in different industrial sectors like automotive and aerospace. Due to the chemical reaction of cross-linking the fabrication is expensive, time consuming and therefore limited to some high-performance applications. The widely used Prepreg and RTM technologies are based on closed or open moulding tools. Despite a possible post-cure step the main part of reaction takes place inside the mould in order to manufacture immediately usable and dimensionally stable parts. Secondary forming of thermoset resins is assumed to be not applicable.

Nevertheless, this contribution demonstrates that the deformation behaviour of a partially cured epoxy system can be significantly extended when a certain range of temperature and an appropriate degree of cure (DOC) are satisfied. Based on a determination of the reaction kinetics and the point of gelation the mechanical properties were analysed by a combination of rheological and tensile tests. Especially the cure behaviour and corresponding mechanical properties in the vicinity of the glass transition were analysed. It was found that an adjustment of the parameters may result in an enormous increase of the deformation potential.

1. Introduction

The manufacturing of fibre reinforced polymer composites is strongly affected by the type of matrix material being used. Thermoplastic polymers offer the possibility of secondary forming. They can be repeatedly heated and re-shaped. Above the melting temperature the material behaviour is viscous and allows a rearrangement of the reinforcing fibres. Thermoset polymers on the other show a substantial and irreversible change of their properties due to chemical curing, which usually takes place at elevated temperatures. Therefore thermoset polymer composites are mainly processed by primary forming technologies like Resin Transfer Moulding (RTM). The final shape of the part is defined in the liquid state of the polymer, before the point of gelation is reached [1]. This is why thermoset manufacturing is often referred to as “wet processing”. This drawback can be turned into an advantage if the mechanical behaviour of gelled, but partially cured networks is analysed and understood [2]. A secondary forming of solid thermosets would enable novel, resource efficient manufacturing technologies for both, thermoset and thermoset composite structures.

The plastic deformation behaviour of thermoset polymer networks has been subject of many research activities in the field of Shape Memory Polymers (SMP). The main focus of these investigations was the determination of suitable deformation and recovery temperatures as well as an analysis of the achievable recovery forces [3, 4]. SMP composites were developed, too, e.g. for compliant applications designed for aerospace technology [5]. Composite material characterisation on the other hand focusses mainly the mechanical behaviour at small strains. It is known that the strain at break increases significantly with temperature [6]. It was often assumed the deformation potential is

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maximised when the polymer is heated above the glass transition temperature [2], whereas a temperature just below the glass transition seems to be more promising for plastic deformation [4, 7]. The presented work analyses the deformation behaviour of an unmodified and partially pre-cured epoxy polymer. The experimental program focused on the influence of time, temperature and degree of cure (DOC). Especially the cure behaviour which is described by a semi-empiric reaction model and the corresponding mechanical properties in the vicinity of the glass transition were analysed.

2. Materials and experimental methods

2.1. Materials and sample preparation

The material investigated is an unmodified epoxy system supplied by Leuna-Harze GmbH consisting of a bisphenol A diglycidyl ether (BADGE) based epoxy resin (Fig. 1) and an isophorone diamine as hardener (Fig. 2), mixed to a ratio of 100:27.7 pbw.

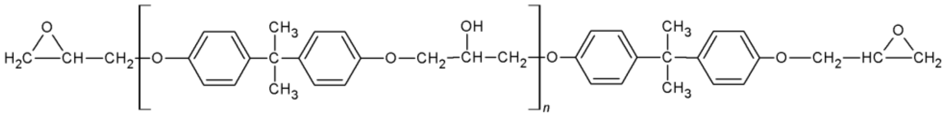

Figure 1. BADGE resin

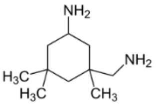

Figure 2. Isophorone diamine hardener

Samples were prepared at room temperature. For differential scanning calorimetry (DSC) and rheometer measurements the samples were cured within the test device in order to investigate the time and temperature dependent reaction mechanism. The resin system was mixed and degassed at room temperature for about 10 min. Pierced Aluminium DSC crucibles with a volume of 40 µl were used. The sample mass varied from 5 to 10 mg. The rheometer scans were performed with a 15 mm plate-plate measuring system under Peltier temperature control. An initial gap distance of 1 mm was chosen. For the tensile tests neat resin plates of the dimensions 500 x 500 x 4 mm³ were manufactured in a RTM moulding tool. The resin was mixed and degassed at 40 °C and subsequently injected into the moulding tool which was pre-heated to the same temperature. Pre-cure took place at 60 °C for 120 min. Tensile specimens were cut according to DIN EN ISO 527-2 (type 1B) with a water jet cutter.

2.2. Experimental methods

DSC scans were performed on a Mettler Toledo 700/1, using nitrogen as purge gas and a purge rate of 20 ml/min. For modelling the kinetic reaction DSC scans with heating rates from 1 to 10 K/min were used. Further DSC scans were conducted with a heat rate of 5 K/min. An Anton Paar MCR502 device was used for the determination of the gelation behaviour. A frequency of 1 Hz, a deformation amplitude of 1 % and heating rates of 1, 2 and 3 K/min were selected. Tensile tests were conducted with a Zwick Z 250 using a temperature chamber and hydraulic clamps. A constant test speed of 2 mm/min was selected.

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3. Results

3.1. Curing kinetics

The DOC serves as an important state variable for polymer description and is described by a formal kinetic model in order to be able to manufacture defined and reproducible specimens. For this purpose the commercial software Thermokinetics was used [8]. The DSC data were used as input for a model-free Friedmann analysis. It allows an estimation of the activation energy and the rate constant. Subsequently a non-linear regression was done in order to find the best fit parameters. One-step and two-step reaction types were taken into account. The best accordance with the experimental data was achieved by using a combination of two autocatalytic reaction mechanisms (Eq. 1). To consider the transition from the chemical dominated to the diffusion dominated state the rate constant k_i is defined by two constituents (Eq. 2). Eq. 3 to 5 describe the model in detail. For glass transition modelling the DiBenedetto equation is used (Eq. 6).

$$\frac{dp}{dt} = k_1[(1+K_{cat1}\cdot p)\cdot(1-p)^{n_1}] + k_2[(1+K_{cat2}\cdot p)\cdot(1-p)^{n_2}], \tag{1}$$

$$\frac{1}{k_i} = \frac{1}{k_{ci}} + \frac{1}{k_{di}}, \tag{2}$$

$$k_{ci} = A_i \cdot e^{\frac{-E_i}{R\cdot T}}, \tag{3}$$

$$k_{di} = A_{di}\cdot e^{\frac{-C_1 T_g^2}{C_2\left(\frac{1}{T}-\frac{1}{T_g}\right)}} \quad \text{for } T < T_g, \tag{4}$$

$$k_{di} = A_{di}\cdot e^{\frac{C_1(T-T_g)}{C_2+T-T_g}} \quad \text{for } T > T_g, \tag{5}$$

$$T_g = T_{g0} + \frac{(T_{g\infty} - T_{g0})\lambda\alpha}{1-(1-\lambda)\alpha}. \tag{6}$$

All coefficients are given in Table 1 and 2.

Table 1. Parameters of the chemical part of the reaction

$log(A_1)$ [s^{-1}]	E_1 [kJ/mol]	n_1 [-]	$log(K_{cat1})$ [-]	$log(A_2)$ [s^{-1}]	E_2 [kJ/mol]	n_2 [-]	$log(K_{cat2})$ [-]
5.1269	59.4192	2.5533	1.221	0.7281	31.5477	0.7123	0.6393

Table 2. Parameters of the diffusion part of the reaction and DiBenedetto constants

$log(A_{d1})$ [s^{-1}]	$log(A_{d2})$ [s^{-1}]	C_1 [-]	C_2 [1/K]	T_{g0} [°C]	$T_{g\infty}$ [°C]	λ [-]
5.6794	-3.6637	7.8152	55.2345	-38	145	0.38

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The resulting model prediction is depicted in Fig. 3.

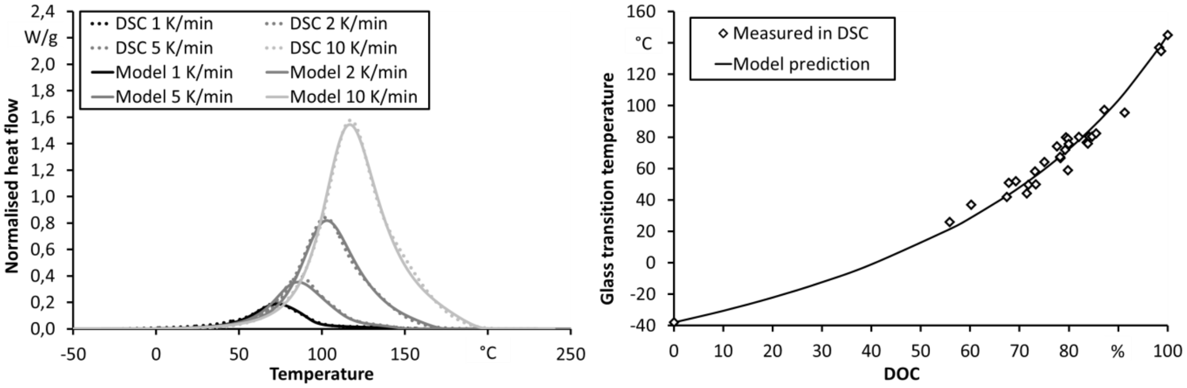

Figure 3. Comparison of experimental DSC data and the model prediction (left) and the development of the DOC dependent glass transition temperature (right)

3.2. Point of gelation

The determination of the point of gelation is of special importance defining the minimum DOC for mechanical tests. Rheological experiments are particularly suitable for this purpose because they provide accurate monitoring of time, temperature and corresponding mechanical properties. Instead of using the common rule *G' = G"* for gelation determination the development of the normal force is evaluated during curing [9]. To ensure this the rheometer was operated in gap control mode, keeping gap distance constant. In consequence the cure induced shrinkage caused a sudden increase of the normal force. In order to connect the elapsed time and temperature history to a DOC the previously described reaction model was used. Three different heating rates were used for data acquisition. Fig. 4 depicts the storage modulus development and the calculated DOC as well as the resulting point of gelation.

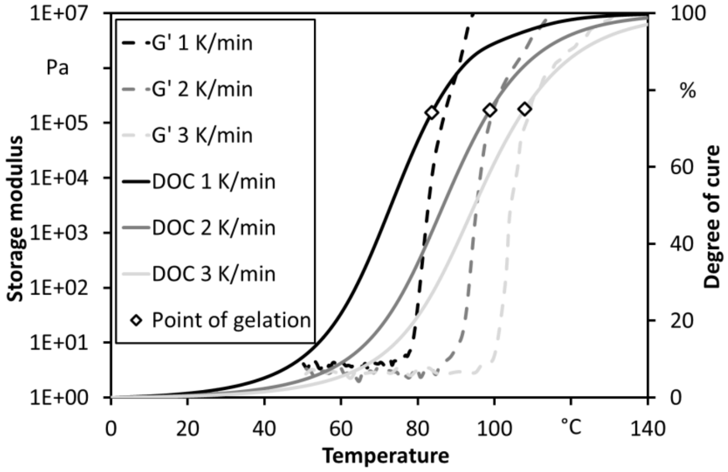

Figure 4. Determination of the point of gelation by rheological experiments

The measured and calculated results are given in detail in Table 3.

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Table 3. Determination of the point of gelation

Heating rate (K/min)	Gelation temperature (°C)	Calculated (Eq. 1) DOC at the point of gelation (%)
1	85.4	0.77
2	98.8	0.75
3	107	0.74
Mean value		**0.75**

It can be concluded that the pre-cure of the epoxy system should reach at least 0.75 in order to reach gelled state. The glass transition temperature at this DOC is about 60 °C (see Fig. 3, right).

3.3. Tensile tests

The tensile test specimens were post-cured in an oven in order to generate defined DOC. Based on the described DSC and rheometer tests and with the help of the kinetic reaction model three different cure cycles where deduced and applied to the specimens (Table 4). They were subsequently verified by DSC scans. To maximise the deformation capability the temperatures for tensile testing should be in the vicinity and just below the glass transition temperature [4, 7].

Table 4. Cure cycles and test temperatures for tensile test specimens

Post-cure temperature [°C]	Post-cure dwell time [min]	Resulting DOC [-]	Test temperature (T - T_g) [K]	Number of specimens
120	60	0.98	RT*	2
120	60	0.98	-5	2
80	60	0.89	-15	2
80	60	0.89	-10	2
80	60	0.89	-5	2
60	120	0.82	-15	2
60	120	0.82	-10	2
60	120	0.82	-5	2

* Room temperature

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For the tensile tests at elevated temperatures the testing machine was heated by a convection oven. The specimens were preheated inside the same oven for 10 min prior to clamping. A thermocouple was applied on the surface of the specimen in order to monitor its temperature. Testing was started as soon as the designated temperature was reached with a deviation of less than ±0.2 K. An individual stress-strain curve for each configuration is depicted in Fig. 5.

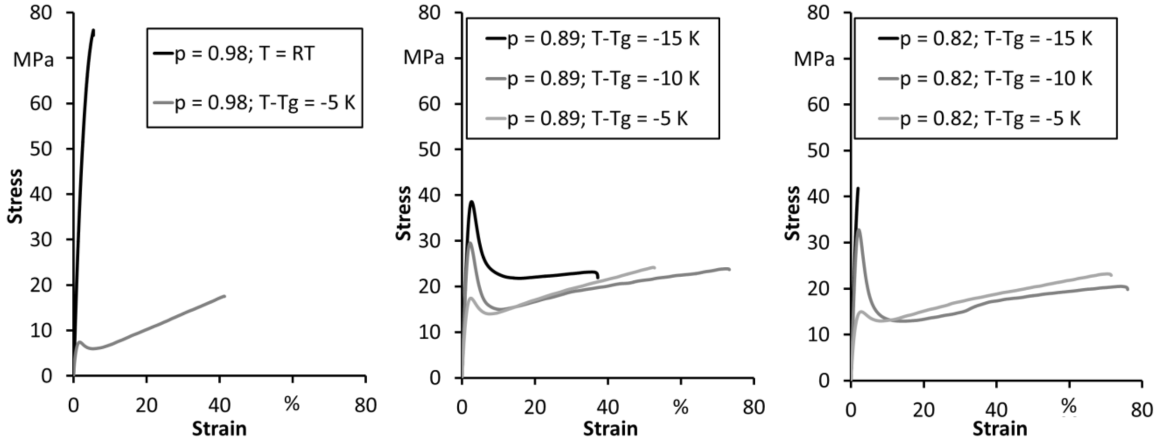

Figure 5. Selected stress-strain curves at p = 0.98 (left); p = 0.89 (centre) and p = 0.82 (right)

As can be seen the fully cured specimen tested at RT does not show a yield point and breaks after a strain of 5.6 %. The stiff and brittle behaviour is typical for an epoxy resin. A temperature increase to T - T_g = -5 K causes a decrease in stiffness, an occurrence of a yield point and a significant increase in strain to more than 40 % (Fig. 5, left). The specimens cured to p = 0.89 (Fig. 5, centre) and p = 0.82 (Fig. 5, right) reveal that the plastic deformation can be further increased by a reduction of the DOC. The specimen with a DOC of 0.82 tested at T - T_g = -5 breaks in the elastic deformation domain. In this case the yield stress is obviously higher than the tensile strength. The highest strain (76 %) could be observed at a testing temperature of T - T_g = -10 K and a DOC of p = 0.82. The yield stress decreases with rising temperature. A comparison of the tensile strains shows a maximum deformation for low DOC (close to or just above point of gelation) and at a testing temperature of T - T_g = *-10 K* (Fig. 6).

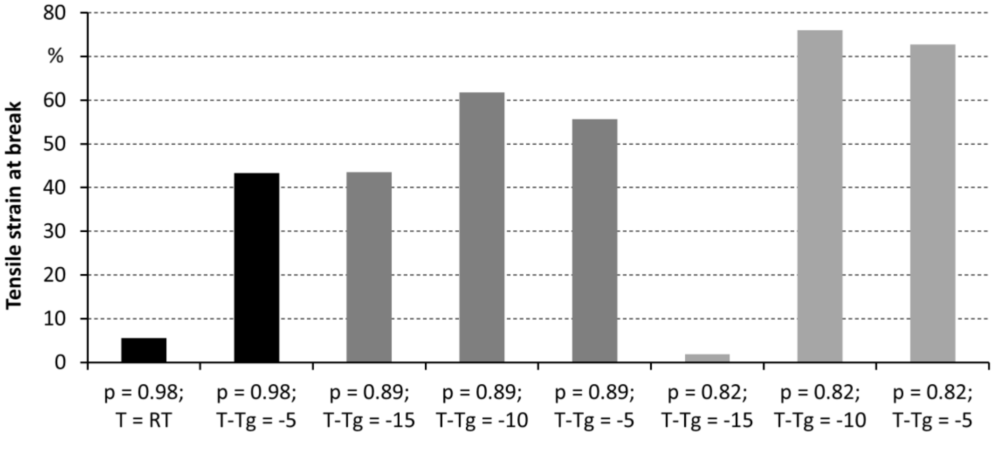

Figure 6. Tensile strain at break in dependence of DOC and temperature

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Regarding the basic idea of using partially cured epoxy polymer as a material for secondary forming it can be summarised that a substantial deformation is definitely possible. The strain applied to the specimen is primarily plastic and remains constant after unloading.

As tests were performed in the vicinity of the glass transition temperature it should be verified that the DOC is not changed due to the elevated temperatures inside the test oven. Therefore DSC samples were cut from each specimen and scanned right after testing. It can be concluded that a temperature of $T - T_g = -5$ K may lead to a small but not negligible amount of post-cure (Table 5) cause an advancement of 0.03 in cure corresponds to a significant increase of the glass transition temperature especially at high DOC (see Fig. 3, right).

Table 5. Post-cure caused by tensile testing at elevated temperatures

Initial DOC [-]	Tensile test temperature $(T-T_g)$ [K]	Amount of post-cure [-]
0.82	-15	0
0.82	-10	0.01
0.82	-5	**0.03**
0.89	-15	0
0.89	-10	0.01
0.89	-5	**0.03**
0.98	-5	0.01

4. Conclusions

It is known that the strain at break of thermoset polymers increases with rising temperature. Still a secondary forming of these materials is not considered as applicable because of their rather brittle behaviour. Based on results from SMP research a test series was designed and performed in order to show that the plastic deformation capability is largely influenced by time, temperature and DOC. For this purpose the reaction kinetics including glass transition temperature and point of gelation were modelled. It was found that an adjustment of the parameters may result in a significant increase of the tensile strain at break. Special attention should be paid to the event of post-cure when a partially cured thermoset network is processed at elevated temperatures. The tests showed that a temperature which is 10 K below the glass transition allows sufficient stability, while at $T - T_g = 5$ K slight but substantial post-cure may occur.

The ability to (re-)shape thermosets was demonstrated. This contribution provides the basis for further investigations of novel forming manufacturing technologies for thermoset based composite materials.

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Symbols

C_1	[-]	WLF constant 1
C_2	[1/K]	WLF constant 2
E_i	[kJ/mol]	activation energy
G'	[Pa]	storage modulus
G''	[Pa]	loss modulus
k_i	[s^{-1}]	rate constant
$log(A_i)$	[s^{-1}]	chemical pre-exponential factor
$log(A_{di})$	[s^{-1}]	diffusion pre-exponential factor
$log(K_{cati})$	[-]	auto-catalytic constant
n_i	[-]	reaction order
p	[-]	degree of cure (DOC)
R	[J/molK]	universal gas constant
T	[°C]	temperature
T_g	[°C]	glass transition temperature
T_{g0}	[°C]	initial glass transition temperature
$T_{g\infty}$	[°C]	final glass transition temperature
t	[s]	time
λ	[-]	DiBenedetto constant

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