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# Effect of cure cycle on enthalpy relaxation and post shrinkage in neat epoxy and epoxy composites

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ABSTRACT

The effect of cure cycle on enthalpy relaxation and warpage is studied for both neat epoxy and glass/epoxy composites. An approach for determining the enthalpy relaxation in the matrix of composite materials combining modulated differential scanning calorimetry and thermogravimetry is presented. The enthalpy relaxation is coupled to structural dimension changes upon reheating by performing modulated thermo mechanical analysis. The enthalpy relaxation is affected by the cooling rate and the presence of the fibrous reinforcement, but is unaffected by variation between a 1-stage and 2-stage cure cycle. Enthalpy recovery is found to exert a minor impact on the sample dimension during reheating since a non-reversing shrinkage is observed during reheating. This shrinkage is ascribed to structural changes on molecular level in the specimen and it is inferred that samples with a high initial disorder only exhibit a small dimensional change during reheating due to structural restrictions within the amorphous polymer network.



## 1. Introduction

Through decades, various authors have shown that ageing of polymers affects the mechanical properties [1–8], density [9], thermal expansion coefficient [10] and water absorption behaviour [10]. Ageing is commonly carried out by heating the amorphous material to a temperature around its glass transition temperature ($T_g$), where the available number of atomic configurations allows atomic rearrangement [11,12]. The atomic configuration in the amorphous material corresponds to the frozen-in structure at the so-called fictive temperature ($T_f$) [13,14], where $T_f$ is a monitor of the energy landscape of the amorphous material [15,16]. Besides affecting $T_f$ through a post annealing step, the temperature at which the atomic structure freezes in can be controlled through the cooling rate from the cure or melting temperature [17]. The atomic rearrangement rate depends on the temperature and thus the cooling rate through the glass transition region impacts the rearrangement extent.

Calorimetric studies on ageing in neat polymers have shown that the relaxation time depends on various parameters such as temperature [18], degree of crosslinking [19,20], degree of cure [21] and mix ratio [22]. In addition to these polymer parameters, the ageing and relaxation in composites are affected by the interaction between the matrix and the fibre reinforcement. The fibres are commonly sized to make them compatible with the matrix by establishing a chemical linkage between the two macroscopic phases. The bonding from the matrix to the sizing on the fibres is considered to confine the configurational arrangements within the matrix and is therefore believed to impact the relaxation behaviour of the matrix.

Determination of $T_f$ and thereby the energy landscape is commonly carried out by means of the enthalpy matching approach [17] where the enthalpy recovery, i.e., the enthalpy gain of the material upon reheating is measured. In addition to the enthalpy matching approach, simpler methods such as direct reporting of the relaxation endotherm at the glass transition can also be applied to address the extent of ageing [23]. The enthalpy matching approach is directly applicable to neat polymers, but faces challenges in determination of the energy landscape in polymer matrices in composites. The heat flow in a differential scanning calorimetry (DSC) measurement on a composite material reflects both the matrix' and fibrous reinforcement's calorimetric response. The presence of the fibrous reinforcement suppresses the recovery endotherm and alters its appearance in the DSC spectrum not only impeding determination of the absolute enthalpy, but also relative comparison between composites with varying reinforcement content. A potential route to circumvent the influence of the fibrous reinforcement on the matrix enthalpy response is to utilise modulated DSC (MDSC). The absence of transitions in most fibrous reinforcements in the relaxation temperature domain of the matrix leaves any non-reversing signals around the matrix glass transition temperature to be ascribed to enthalpy recovery. In this work, quantification of the influence from the cure cycle on the enthalpy relaxation in neat epoxy and epoxy laminates is carried out. MDSC is used in order to provide a method for quantification of enthalpy in laminates and to elucidate the impact from the fibrous reinforcement on the relaxation and the cure cycle. The cure

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cycle has previously been reported to affect other laminate properties such as material straining and stiffness response [24–27]. In addition, the coupling between enthalpy relaxation and the thermo mechanical response of the material is explored.

## 2. Materials and methods

### 2.1. Materials

The employed epoxy consisted of a DGEBA base with monoreactive diluents and a curing agent consisting of an aliphatic polyether amine denoted XTJ-568 (major component) and isophorone diamine (minor component). The two components constituting the epoxy systems were mixed in the stoichiometric ratio. The fibre reinforcement used in the study was epoxy sized *E*-glass with a fibre diameter of less than 17 μm. The fibre weight fraction of the composite laminate has been measured to 65 wt%, which compares to a volume fraction of 44 vol%.

### 2.2. Methods

Both neat epoxy and single ply laminate samples were prepared. For the laminate, a unidirectional epoxy compatible glass fabric was wetted with the epoxy at atmospheric pressure prior to the cure cycle. Both the neat epoxy and the laminate samples were cured by means of 4 different cure cycles. One and two step cure cycles were utilised: In the one step process, the samples were inserted directly into a preheated oven at 85 °C and remained there for 5 h. In the two step cycle, the samples were allowed to set at room temperature overnight followed by a post cure at 85 °C for 5 h. The samples were cooled from 85 °C to room temperature at a rate of either 10 °C/h (slow) or were quenched by pressing a precooled (−18 °C) metallic piston onto the surface of the sample (quench). With the quenching procedure, the sample reached room temperature within about 10 s, i.e., the average cooling rate was around 400 °C/h. As the samples have been cured at the same temperature, but exerted to different cooling rates, they have been exerted to a different relaxation time and should thus exhibit different energy states and the samples should therefore exhibit a different enthalpy relaxation upon reheating. Samples subjected to the one and two step cure cycle had the same $T_g$ and the thickness of the neat epoxy and the laminate sample is similar.

#### 2.2.1. Modulated DSC

The MDSC measurements were performed on a TA Q2000 DSC at a heating rate of 4 °C/min, an amplitude of 2 °C/min and a period of 60 s up to a temperature of 110 °C in a nitrogen atmosphere. For each sample, 5 MDSC measurements were performed. After performing the DSC measurements, the DSC crucibles of the 5 composite samples exerted to a given cure cycle were opened and the samples were transferred to an alumina thermogravimetry cup and inserted into a Netzsch 449 F3 Jupiter STA. The thermogravimetry (TG) measurement was conducted in an air atmosphere with a purge rate of 20 mL/min and the sample was heated to 750 °C at a rate of 5 °C/min and this temperature was maintained for 30 min which allowed complete combustion of the matrix phase. The weight loss used to determine the fibre content of the sample was taken as the difference between the initial sample weight and the weight after completion of the 750 °C isothermal step.

#### 2.2.2. Modulated TMA

Samples for thermomechanical analysis (TMA) were prepared by utilising the same cure cycles as described in the above. Mixed resin was filled into a 5 mm diameter silicone hose closed with a clamp at one end by using a pipette. To prepare a sample with laminate characteristics a glass roving was drawn through the silicone hose and after clamping one end of the hose, the mixed resin was filled into the hose. After adding the mixed resin and removing any bubbles in the hose by squeezing them out, the hoses were straightened and kept in this position throughout the curing process to ensure a fixed sample geometry. After cure the samples were cut into a height of 6–7 mm and measured on a TA Q400EM TMA. The temperature was initially equilibrated at 20 °C for 30 min to ensure a uniform temperature of the samples. The samples were measured in modulated mode with a heating rate of 1 °C/min, an amplitude of 5 °C and a period of 300 s in the temperature range 20 to 120 °C. Three measurements were performed for each sample. During the measurements, the dimensional change in the fibre direction was recorded as a function of temperature. The 1 stage slowly cooled specimen samples were also exerted to a dual heating procedure in the TMA: The heating procedure was similar to that described above and after completion of this, the samples was cooled at either 30 or 5 °C/h to room temperature followed by another up-scan at the sample conditions as the first one.

## 3. Results and discussion

During the modulated DSC scan, an endothermic response with an onset around 47 °C, which is around 27 degrees below the $T_g$ value of 74 °C (see reversing signal) is found in the non-reversing signal (Fig. 1). A $T_g$ of 74 °C implies that the matrix has been in a devitrified state throughout the curing process as the curing has been performed at 85 °C. As exothermic events are absent in the DSC spectrum up to 110 °C, no post cure is occurring during the DSC measurement and this suggest that the monomers have been reacted and this is supported by earlier measurements on this epoxy system that have found that a degree of cure of 95–98% can be achieved at 85 °C [24]. The observed endotherm is ascribed to enthalpy recovery due to enthalpy relaxation due cooling from the cure temperature and it continues until a temperature of 84 °C, which is 2 °C above the end of the glass transition. As the example in Fig. 1 is a one stage cured slowly cooled neat epoxy sample, there is a large endothermic response during the upscan, which causes a discrepancy between the total and reversing heat flow signal. Consequently, from the $T_g$ of the sample determined from the total heat flow signal is 65 °C, which is 9 °C lower than that determined from the reversing signal. This highlights the importance of importance of measuring $T_g$ of samples with a unified thermal history if this has brought the sample far from equilibrium [28].

The heat absorbed by the sample due to enthalpy recovery, has an asymmetric shape showing the strong temperature dependence of the relaxation time [29,30]. Comparison of the three heat flow signals reveals that the sub-$T_g$ enthalpy recovery inflicts a sloping baseline for the total heat flow curve prior to the glass transition and consequently, $T_g$ determined from the total heat flow signal is lower than that from the reversing heat flow signal. In polymers, normally α and β-recovery can be observed, where the β-recovery occurs at lower temperatures than α-relaxation as it involves localised rearrangements. In Fig. 1, only one

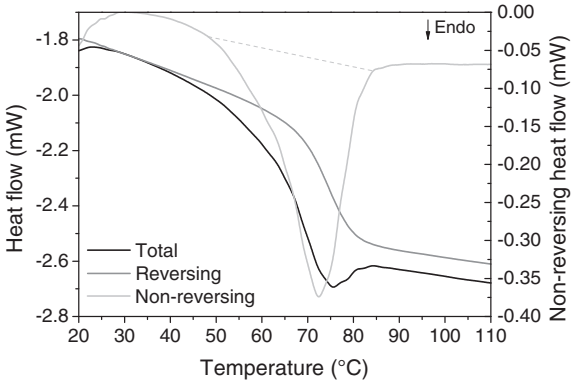


**Fig. 1.** MDSC spectrum of a one stage cured slowly cooled neat epoxy sample showing the total and reversing heat flow (left axis) and the non-reversing heat flow (right axis). The integrated area used to determine the enthalpy recovery from the non-reversing signal is shown by the dashed line.