PHYSICAL AGING IN THERMOSET RESINS

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ABSTRACT

In recent years, advanced thermoset matrix composite manufacturers have turned to increasingly complex and optimized cure cycles; in support of these new cycles, there has been the increasing use of process simulation to successfully overcome the many challenges. These simulation efforts are based on current state-of the art modelling, where the matrix state is defined uniquely in terms of the instantaneous degree of cure and temperature. However, it is increasingly clear that one area that still requires careful scrutiny is the effect of physical aging. Physical aging is when the glassy material attempts to reach the thermodynamic equilibrium state, and is accompanied with a reduction in thermodynamic properties. In this work, a commercial epoxy system commonly used in aerospace applications has been examined with respect to this phenomenon of physical aging during cure. TMDSC experiments confirm that physical aging during an isothermal dwell retards the re-initiation of the residual cure reaction in a partially cured resin. A significant new finding is that physical aging changes the dynamics of the polymer chains in the glass transition region, causing a sharpening of the T_g transition, and potentially explaining previous discrepancies between experiments and modelling for complex cycles. This suggests the need to upgrade current models to include physical aging to increase their reliability and accuracy.

1 INTRODUCTION

This work presents results which quantify the effect of physical aging on a thermoset epoxy resin during cure. For the first time, a toughened, amine-cured epoxy resin system, Hexcel 8552, was conditioned and then characterized systematically from the viewpoint of physical aging. Samples of Hexcel 8552 neat resin were partially cured for a range of elevated temperatures and different times and characterized by Modulated Differential Scanning Calorimetry (MDSC). MDSC results reveal that physical aging during cure alters the shape of the residual heat of reaction peak. Heat capacity measurements also show that physical aging modifies the glass transition dynamics, as shown by the narrower glass transition regions of aged samples in heat capacity space. The results of this work can be used in developing more reliable cure kinetic models for use in predicting and controlling the manufacturing of advanced composite parts.

Fibre reinforced polymer matrix composites are well-established as structural materials of choice in aerospace, wind energy, sports equipment, and increasingly automotive and other sectors. Their desirability comes not just from the superior properties of the materials, but also from the ability to tailor the fibre orientations and produce the finished product in essentially one step with an in-situ process, allowing geometries, shapes, and sizes which are unachievable with traditional metallic materials. However, although their structural performance and design freedom is well appreciated, the need to reduce manufacturing cost and risk remains a major barrier to further adoption of these materials. The ability to build large and complex products with an in-situ process is a double-edged sword, as the resulting manufacturing complexities require good control of the process to achieve the desired quality at the anticipated cost and rate. One approach to managing manufacturing complexity is process modelling or simulation, which has gained increasing success in the last two decades.

In this paper, we focus on thermoset matrix composites. It is well understood that the thermoset resin undergoes a significant transformation during the manufacturing process: the low-molecular-weight uncured resin transforms to a solid and stiff matrix of high crosslink density by a chemical reaction, typically known as the cure reaction. In the literature, progress in the cure reaction is gauged by the degree of cure (DoC), commonly represented by the number of bonds transformed, and typically measured using the heat of reaction measured in a Dynamic Scanning Calorimeter (DSC) [1].

Typical current modelling practice is to describe thermochemical, physical and mechanical properties of the transforming composite structure as a function of combination of manufacturing process parameters. Among these properties, cure rate [2], rubber-glass transition temperature (T_g) [3], [4], viscoelastic properties [5], coefficient of thermal expansion (CTE) [6]–[9], heat capacity [10], and cure shrinkage [7], are described as a function of Degree of Cure (DoC) and cure temperature T. DoC can be considered as an intrinsic state variable which itself is a function of cure temperature and cure time. On the other hand, temperature is an extrinsic independent parameter. In short, currently, the state of the art in modelling of thermoset resin property evolution, absent complexities such as particle tougheners [11], [12], is that all properties are a function of just two state variables: DoC and T. This has worked quite well, but there have always been indications that other state variables may, at times, be at play.

In this work we show that, in addition to DoC and cure temperature T, the phenomenon of physical aging can also play a key role in the evolution of properties throughout the cure reaction.

2 PHYSICAL AGING

When cooling a polymer from elevated temperatures, initially molecules have enough thermal energy and mobility to change their conformation by segmental motions. Therefore they can accommodate to the applied cooling rate. This implies that the polymer material is in its thermodynamic equilibrium state at temperatures above T_g, and the thermodynamic properties of the material – at a given temperature and pressure - are not time-dependent.

On the other hand, at temperatures below T_g, the thermal energy of the polymer chain is not adequate to maintain the segmental motions. This results in a frozen structure, which leads to the glassy behavior of the material. Once the glass is formed, the polymer molecules reach the non-equilibrium state. Similar to every system experiencing a non-equilibrium state, the glassy material endeavors to reach the equilibrium state over time. The evolution of the amorphous glassy material towards the thermodynamic equilibrium state is known as physical aging.

As can be seen in Figure 1, given insufficient mobility of the polymer chain segments in the glassy state, the material carries excess thermodynamic properties. During physical aging, the excess properties relax over time, and given long enough time, the material is able to reach the equilibrium state. Hence, the physical aging phenomena is accompanied by reduction in thermodynamic properties, such as volume, enthalpy and entropy [13].

It is well known that physical aging increases the viscoelastic timescale of polymers [14], increases the stiffness and reduced the toughness of the polymer [15], and deteriorates the permeability of polymeric thin films and membranes [16].

In contrast to thermoplastics, the scientific work performed on thermosets is far from abundant. Among those, Odegard and Bandyopadhyay [17] reviewed the physical aging of epoxy polymers and their composites. The majority of researchers have investigated fully cured thermoset systems, with only a few exceptions. For examples, Lee and McKenna [18] studied the physical ageing of polypropylene oxide/DGEBA networks with different crosslink densities. They concluded that the time needed to reach equilibrium increases with increase in crosslink density. In another study, Wang and Gillham [19] explored the physical aging behavior of a high-temperature, amine/ epoxy thermosetting system using the Torsional Braid Analysis (TBA). Different specimens were cured to different DoCs and were aged at different aging temperatures. Their work revealed that the segmental mobility, which is a required factor in physical aging, is independent of the extreme changes of chemical structure (as changing by the extent of cure). As mentioned before, in composites processing, the thermoset resin transforms from an uncured, viscous fluid to a rubbery gelled network, and then upon vitrification, it forms a rigid glassy material [20] which is thermodynamically out-of-equilibrium and is prone to physical aging. As a result, to be able to fully predict and control the behavior of advanced thermoset composite structures during storage, manufacturing and in service, current modelling approaches should be updated to ensure they are able to include the effects of physical aging on the evolving properties of the matrix.

In this work, for the first time, we methodically examined a toughened, amine-cured epoxy resin with regard to physical aging phenomena. Different specimens of Hexcel® 8552 were cured at a temperature of 120°C for different elongated cure times ranging from 4 to 10 hours. This approach resulted in partially cured samples of differ

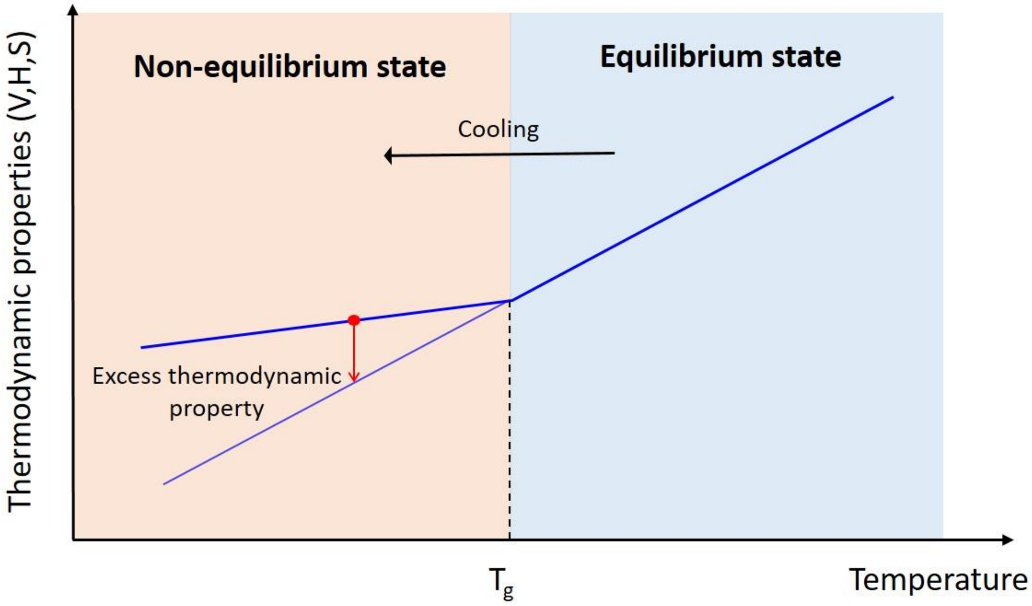

Figure 1. Evolution of the thermodynamic properties upon cooling from above Tg

extents of cure and physical aging .Then, the sample were scanned using Temperature Modulated Differential Scanning Calorimetry (TMDSC), and physical aging occurring in the isothermal curing/aging step were determined by scanning in a following heating ramp.

3 METHODOLOGY

Materials

Throughout this work, Hexcel 8552 neat resin in the form of a thin film has been used. This system includes a mixture of two multifunctional epoxy resins: tetraglycidylmethylenedianiline (TGMDA) and triglycidyl-p-amin-ophenole (TGAP); diaminodiphenysulfone (DDS) is used as hardener. The matrix is also toughened with poly (ether sulfone) (PES) thermoplastic, which is fully dissolved [21]. To prepare the specimen, the resin film was thawed at room temperature for 30 minutes. Then the degassing procedure was performed in a Vacuum Oven at 60°C for two hours. Cure kinetics simulations using Raven simulation software [22], with the Hexcel 8552 material model [23] have shown that the degassing procedure does not contribute to advancement of cure in the resin.

TMDSC Measurements

The physical aging behavior of the epoxy resin system was characterized using a TA Instrument Discovery DSC 2500. The equipment was calibrated using indium and synthetic sapphire as standard materials. Samples of neat 8552 resins, each weighing 6 ± 1 mg were put in aluminum hermetic pans and sealed. The initial temperature of the DSC was set to 40°C. Specimens were cooled down to -50°C at a constant rate, then the temperature rapidly increased to 120°C (aging temperature; T_a). The samples were isothermally conditioned at T_a for various periods of time, from 4 hours to 10 hours. After the isothermal step, the samples were quenched to 0°C. In the next step, the specimen were scanned in a heating cycle at the rate of 2°C/min, followed by a second similar quenching and heating scan. The modulation period and amplitude were set as 60S and 1°C, respectively. The glass transition temperature was obtained at half height of the step change in the revesing heat capacity as a function of temperature. In all the experiments, the DSC cell was purged by Nitrogen gas at the rate of 50 ml/min. The T_g of the uncured thermoset resin (obtained from the initial cooling scan) is - 1.62 ± 0.84 °C.

4 Results

As has been shown in the literature, e.g. [13]–[15], [17], upon heating from temperatures well below T_g, an endothermic peak caused by physical aging is expected. As can be observed from figure 1, the endothermic peak can be observed on the non-reversing heat flow signal gathered in the first heating scan for the 8552 specimens. The endothermic peak is followed by an exothermic residual heat of reaction, which reflects the fact that the 120°C isothermal hold does not fully cure the samples. Starting from the hold time of 4hr, no endothermic peak is observed, indicating that this time period is not long enough for the sample to develop physical aging during the hold step. At 6hr of isothermally heating the sample at the constant temperature of 120°C, physical aging develops and the endothermic peak appears on the consequent heating scan. With increasing hold times of 8hr and 10hr, the area of the endothermic peak increases and the peak shifts to higher temperatures. These trends agree well with the literature.

The magnitude of the endothermic peak is obtained by extrapolating the non-reversing heat flow signal of the glassy region to the glass transition temperature and beyond. The area between the recorded signal and the extrapolated glassy heat flow is calculated and reported as enthalpy of aging (ΔH_a). The Values of ΔH_a for each hold time is presented in Table 1. As seen in Table 1, the enthalpy of aging has an increasing trend with hold time. Consequently, the magnitude of the endothermic peak recorded on the heating ramp can be considered as the extent of physical aging developed in the previous dwell step in the samples. Another significant finding revealed by the DSC experiments is that the shape of the residual exothermic peak alters with different hold times. As can be seen from figure 1, the kick-off reaction temperature, the temperature at which the cure reaction initiates again, shift to higher temperatures with an increase in hold time. Thus, we can conclude that physical aging can interfere with kinetics of cure reaction. This is consistent with previous observations with other materials [24], [25].

Figure 2 presents the reversing heat capacity of the samples as a function of temperature in the first heating scan after the dwell step. Careful observation shows that the slope of the reversing heat capacity signal in the glass

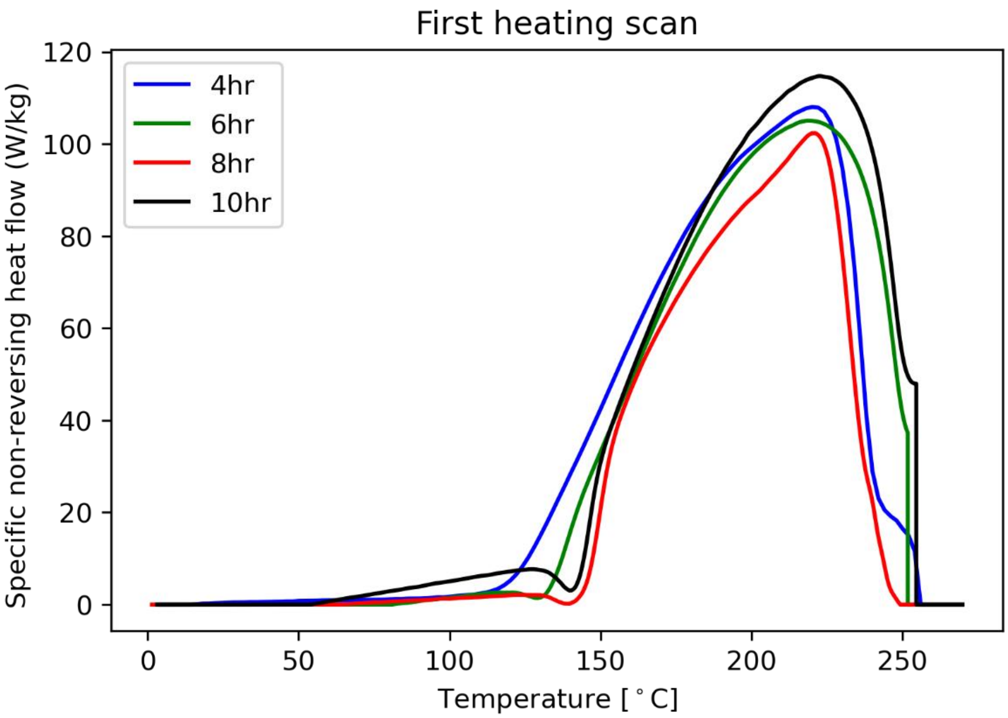

Figure 2. Specific non-reversing heat flow of Hexcel 8552 samples cured at 120°C for different periods of time as a function of temperature

Table 1. Enthalpy of aging and glass transition temperatures of Hexcel® 8552 samples, aged at 120°C for different aging times

Hold time (hr)	Enthalpy of aging (J/g)	T_g (°C)
4	0	120.12
6	0.49	134.05
8	0.76	144.24
10	1.52	143.36

transition region increases with dwell time. This observation signifies that the physical aging evolved during the isothermal hold at 120°C has modified the dynamics of the glass transition temperature in subsequent heating from glassy state. This observation has not previously been reported in the literature for physical aging of thermosetting materials. It is of importance because the current approach to materials characterization of advanced composite resins treats the glass transition as being of fixed shaped, and represented by a single value, often captured by the half height method. Results presented here indicate that with increasing physical aging, the glass transition narrows, with subsequent impact on all properties.

With regards to process modelling, this implies that process models used for cycles where physical aging is significant need to incorporate the effects of physical aging on the dynamics of the chains in the glass transition region. As noted above, physical aging is expected to alter the viscoelastic behavior, as well as the volume behavior of the thermoset resin with respect to temperature. In short, the reliability of the models describing the viscoelastic and mechanical properties models involving the volume behavior (e.g., cure shrinkage and CTE) will be adversely influenced if the phenomenon of physical aging is overlooked.

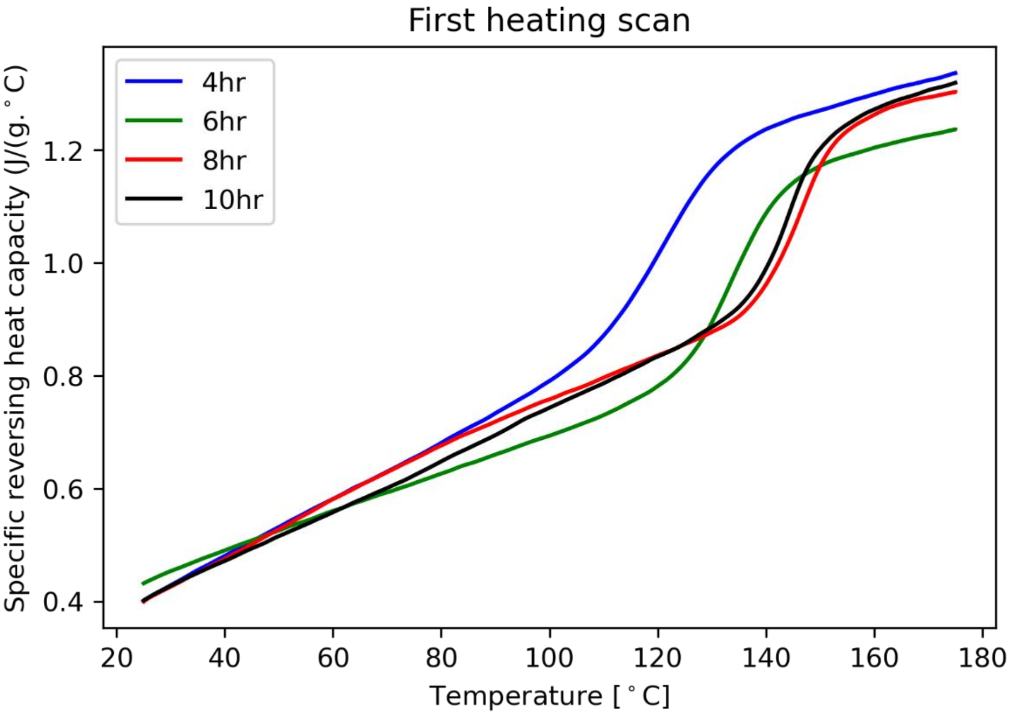

Figure 3. Specific reversing heat capacity of Hexcel 8552 samples cured at 120°C for different periods of time as a function of temperature

5 CONCLUSION

In this study, samples of Hexcel® 8552 thermoset resin were systematically conditioned at an aging temperature of 120°C for different periods of time, from 4 hours to 10 hours. In the isothermal hold step, the material is prone to develop physical aging, once the glass transition temperature exceeds the cure temperature. The indication of physical aging is observed in the following heating scan, in non-reversing heat flow space as well as reversing heat capacity space. The analysis reveals that the magnitude of the endothermic peak, appearing prior to the residual heat of reaction exothermic peak, correlates with the extent of physical aging. The results of TMDSC experiments also show that the cure kinetics of the residual cure reaction is modified by physical aging. In reversing heat capacity space, it is observed that the slope of the reversing heat capacity signal as a function of temperature increases with isothermal hold time. This sharpening effect in the glass transition region implies that the dynamics of the polymer chains in the thermoset network has been modified by physical aging effects. The findings of this work can improve the next generation of process modelling approaches for advanced thermoset composites.

6 REFERENCES

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