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PHYSICAL AGING DURING CURE OF THERMOSET RESIN

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ABSTRACT

Presently, the most effective approach for designing the cure cycle of thermoset matrix composite structures is utilizing cure kinetics modelling to achieve an ideal result. This could entail designing a quick cycle that avoids excessive heat generation (exotherm) or incorporating an intermediate hold period for on/off tool processing. Improved cure cycles and advanced resin chemistries demand improved cure kinetics and corresponding material models. The emphasis of this work is to incorporate the effects of physical aging into these material models to enhance the accuracy of thermoset cure simulation. Physical aging refers to the spontaneous process by which a material in a glassy state tries to return to its original thermodynamic equilibrium condition. The process of physical aging results in a decrease in thermodynamic parameters, such as volume and enthalpy. In this study, a characterization method is proposed to investigate the physical aging behaviour of partially cured thermoset resins. Samples of Hexcel 8552 neat resin were examined using Temperature Modulated Differential Scanning Calorimetry (TMDSC). Resin samples were cured to pre-gelation and post-gelation state in the DSC and then were annealed at two different temperatures for increasing time periods. Physical aging was identified by conducting a subsequent heating scan. The results suggest that including two isothermal holds, namely cure and aging steps, leads to successfully separating the effects of physical aging and residual cure.

1 INTRODUCTION

Fibre-reinforced polymer matrix composites are commonly used as structural materials in industries such as aerospace, automotive, and recreation, as well as the sustainable energy sector. Specifically, the aerospace industry is inclined to implement carbon fibre-reinforced thermoset composites due to their superior mechanical strength, thermal stability, and reduced weight. However, the manufacturing of thermoset composites is complex. A classic manufacturing process includes treating the part at elevated temperatures and pressures for predetermined times in industrial-sized autoclaves [1]. During such a process, the prepreg layers are compacted under high pressures, and elevated temperature activates an exothermic chemical reaction, known as the cure reaction. During this reaction, crosslinks form between polymer chains and cause the uncured viscous material to transform into a stiff and glassy solid, which can perform as a structural component [2].This transition increases the glass transition temperature (Tg) of the material. At a certain time during the process, Tg surpasses the cure temperature, and the material enters the glassy state. As it is well-established, a non-crystallin glassy solid is in thermodynamic non-equilibrium state [3].

Naturally, the material in non-equilibrium state tends to relax toward the equilibrium state. In this case, a reduction in the excess thermodynamic properties such as enthalpy and specific volume is observed. This process is referred to as physical aging. Considering the context of manufacturing of thermoset composites, enthalpy changes induced

by physical aging can alter the kinetics of the cure reaction, and specific volume changes can diminish the desired dimensional stability of the part [4]. On the other hand, Research has shown that specific volume decreases due to physical aging by means of a reduction in free volume entities (voids) within the material [5]. Reduction in free volume leads to a reduction in segmental mobility of the thermoset resin and causes a change in properties such as modulus, coefficient of thermal expansion, and heat capacity.
Nowadays, industries are pushing for more advanced and complex cure cycles. On the other hand, material suppliers constantly introduce new materials. As a result, there is an immediate and constant need to improve the current understanding of thermoset composite materials and update the material models accordingly. Doing so enables process modelers to predict and evaluate process outcomes. The current approaches to thermoset parts manufacturing process modelling describe the evolving properties as functions of temperature and DoC (state variables). Consequently, at a given temperature and DoC, and in the absence of particulate toughening agents [6], the properties of the material remain constant owing to the extremely slow diffusion mechanisms taking over the kinetics of the process. However, the physical aging-induced time-dependent evolution of the properties of the material in the s is inevitable. As a result, to improve the current generation of material models, incorporation of physical aging is necessary.
This work emphasizes the characterization of physical aging in a common thermoset resin system in the aerospace industry in the context of classic cure cycles.

2 Experimental method

2.1 Materials and sample preparation

In this study the thermoset resin Hexcel 8552 neat resin, an aerospace-grade complex resin system, was used. This system includes a mixture of two multifunctional epoxy resins: tetraglycidylmethylenedianiline (TGMDA) and triglycidyl-p-amin-ophenole (TGAP); and diaminodiphenysulfone (DDS) acts as hardener. A thermoplastic polymer (polyether sulfone) acts as a toughening system [7]. Prior to sample preparation, the resin film was thawed at room temperature for 30 minutes. A degassing procedure was performed in a vacuum oven at 60°C for two hours. Cure kinetics simulations using the NCAMP Hexcel 8552 material model [8] have shown that the degassing procedure does not contribute to advancement of cure in the resin. Samples of neat 8552 resins were put in aluminum hermetic pans and sealed.

2.2 Temperature Modulated Differential Scanning Calorimetry

All the temperature cycles described in section 2.4 were performed in a TA Instruments Discovery DSC 2500. The equipment was calibrated using indium and synthetic sapphire as standard materials. The modulation period and amplitude were set to 60 S and 1° C, respectively.
The first set of samples underwent a classic isothermal cure cycle at 120° C for increasing time periods. After the isothermal hold, the samples were quenched to 0°C and scanned in a heating cycle at the rate of 2° C/min.
For the next set of experiments, two groups of neat resin samples were isothermally cured at 150 °CC for 25 minutes and 75 minutes in the DSC. The cure cycles resulted in glass transition temperatures of 55.6±1.3° C and 147.0±1.6° C, respectively. The glass transition temperature was characterized during heating at a rate of 4° C/min and was defined as the half height of the step change in the reversing heat capacity versus temperature. The corresponding degree of cure (DoC) was calculated using equ. (1), in which α , $H(t)$, and ΔH represent DoC, instantaneous heat generated by the cure reaction, and total heat of the cure reaction, respectively.

$$\alpha = \frac{H(t)}{\Delta H} \quad (1)$$

The properties of the samples cured according to the cure cycles above are represented in Table 1. After the cure step, the temperature was decreased to different aging temperature. Thermodynamic driving force (degree of undercooling, ΔT in Table 1) was kept constant when selecting the aging temperatures. The samples were aged at aging temperatures for increasing time periods, from one to 10 hours. Glass transition temperature and the endothermic peak associated with physical aging are identified by the subsequent heating scan.

Table 1-Properties of the samples used in this work

Sample	Network structure	Tg (°C)	DoC	Ta (°C)	$\Delta T = T_g - T_a$
8552-pre-gel	Before gelation	55.6±1.3	0.29±0.01	40, 50	~ -16, -6
8552-post-gel	After gelation	147.0±1.6	0.65±0.01	130, 140	~ -17, -7

3 Results

3.1 Temperature modulated DSC

The 8552 samples were cured at 120° C and the DSC results of the subsequent heating scans at 2° C/min are illustrated in **Error! Reference source not found.**. Physical aging developed in the material due to annealing below Tg is erased when temperature rises above Tg, which is commonly known as rejuvenation. It is well established that rejuvenated appears as an endothermic peak in the heat flow measured by the DSC [9], [10]. The endothermic peak associated with physical aging can be observed in the DSC graphs of the samples aged at 120° C. as one can see in the inset of **Error! Reference source not found.**, with increasing hold time from 4 to 10 hours, the area of the endothermic peak increases. The aging enthalpy associated with the endothermic peaks increases from 0 (no endothermic peak) for 4 hours to 1.52 J/g for hold time of 10 hours [4]. As can be seen from **Error! Reference source not found.**, the appearance of the endothermic peak associated with physical aging alters the shape of the residual cure exothermic peak. The kick-off reaction temperature, the temperature at which the cure reaction initiates again, shifts to higher temperatures with an increase in hold time.

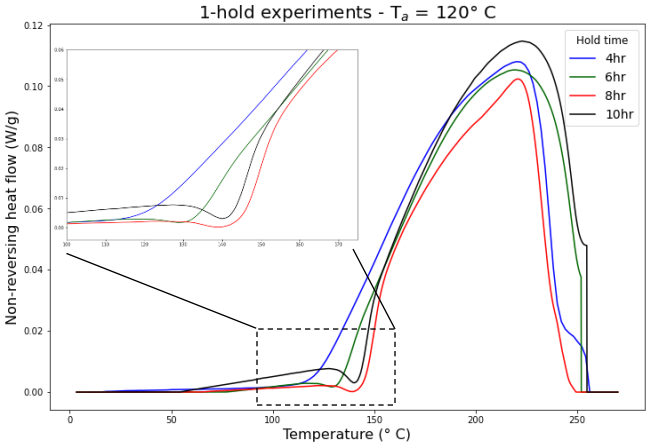

Figure 1- DSC results of 8552 samples cured at 120° C as a function of aging time – heating cycle at 2° C/min

Thus, we can conclude that physical aging can interfere with kinetics of cure reaction. Due to the interaction between rejuvenation and residual cure reaction, the study of physical aging alone and its separation from the cure reaction remains unresolved. This further emphasizes the importance of developing a characterization method to successfully overcome this issue.

The non-reversing heat flow signals of samples at pre-gelation aged at two different aging temperatures are shown in **Error! Reference source not found.**. As can be seen in **Error! Reference source not found.**, the endothermic peak associated with physical aging appears at around 52 °C for the sample aged at 40 °C for one hour. The endothermic peak temperature shifts to higher temperatures with an increase in aging time. With increasing the aging temperature to 50 °C, the endothermic peak temperature shifts to slightly higher temperatures in constant aging time. The evolution of the endothermic peak temperature of the sample with aging time is presented in Figure 3 (a). A method for obtaining the enthalpy of aging, using the area under the DSC curves, has been proposed before [4]. As can be seen in Figure 4, the aging enthalpy of 8552 samples aged at 40° C and 50° C has an increasing trend with aging time. On the other hand, with increasing aging temperature from 40° C to 50° C the aging enthalpy reduces.

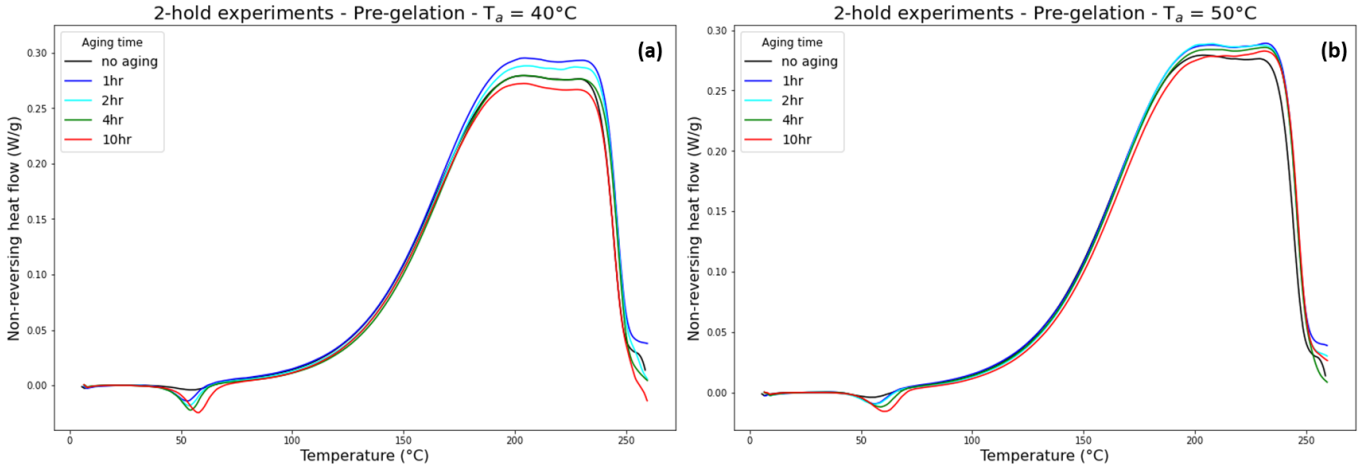

Figure 2- DSC results of 8552 samples at pre-gelation state (DoC=0.29) as a function of aging time, (a) aged at T_a = 40° C (ΔT≈-16° C); and (b) aged at T_a = 50° C (ΔT≈-6° C) – heating cycle at 4° C/min

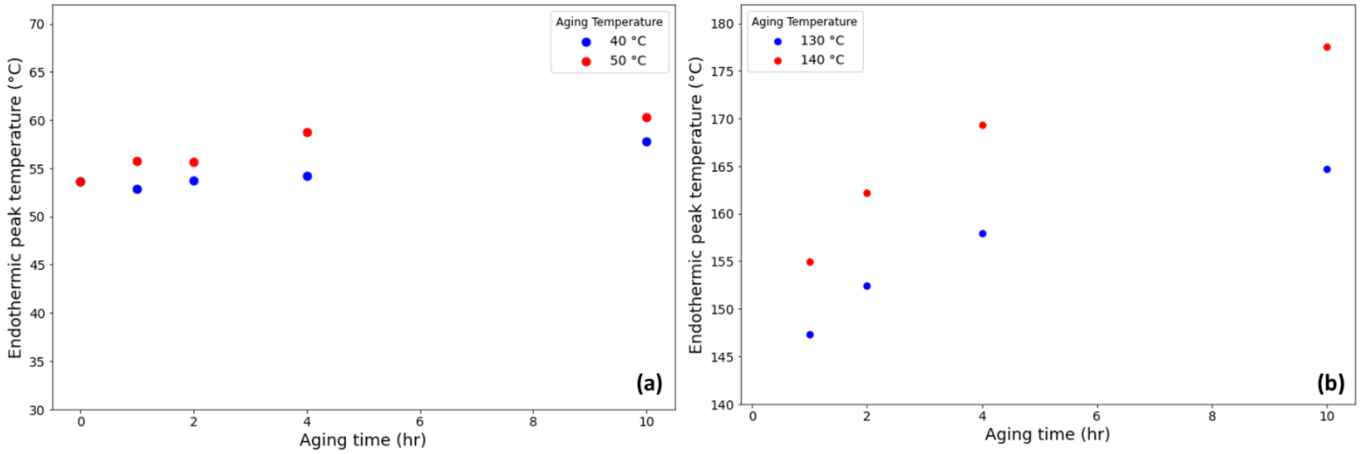

Figure 3- Endothermic peak temperature of 8552 samples (a) at pre-gelation and (b) at post-gelation, as a function of aging time

The most interesting observation is that when the system is in the pre-gel state, physical aging and the residual cure reaction are fully separated. As can be seen in **Error! Reference source not found.**, the cure reaction kick-off temperature of the samples remains constant with physical aging. This means that while the physical aging (or its aftermath, rejuvenation) is very far from the re-initiation of the residual cure reaction, the kinetics of the cure reaction remain unaltered by physical aging. This proves that the proposed characterization method can be used to separate physical aging and cure.

Figure 4 demonstrates the non-reversing heat flow signals of samples at post-gelation aged at two different aging temperatures. As can be seen, physical aging and the residual cure reaction are convoluted to a great extent. With increasing aging time from 1 hour to 10 hours, both the shape of the residual cure exothermic peak and the cure reaction kick off temperature are affected. Similar to samples aged at their pre-gel state, the endothermic peak temperature and the magnitude of the endothermic peak both increases with physical aging. Figure 5 describes the trends of the endothermic peak temperature and enthalpy of aging with increasing aging time.

As it is clear from Figure 4, when the samples undergo physical aging in post-gel state, due to the limited distance between Tg and the cure reaction kick-off temperature, physical aging and the residual are significantly convoluted.

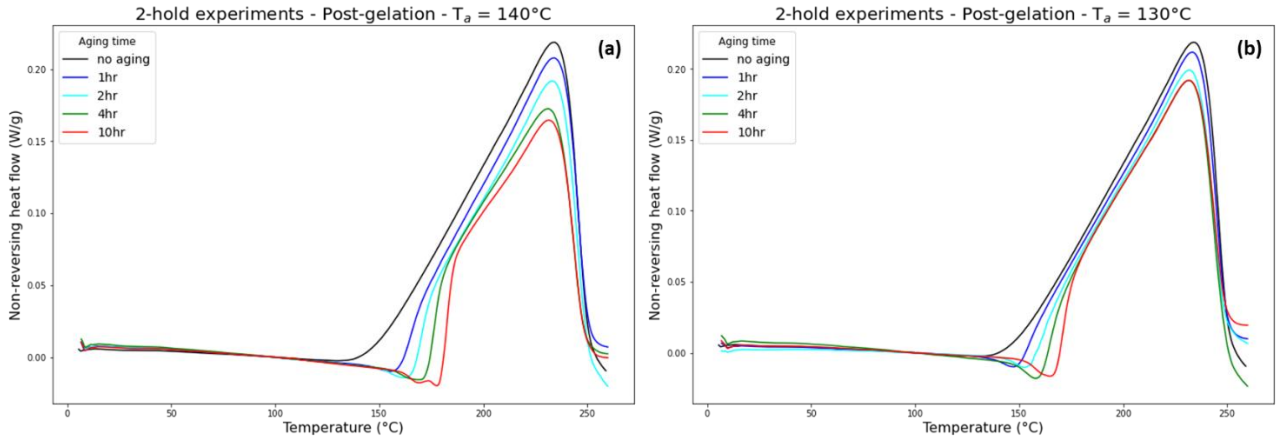

Figure 4- DSC results of 8552 samples at post-gelation state (DoC=0.65) as a function of aging time, (a) aged at T_a = 130° C (ΔT≈-17° C); and (b) aged at T_a = 140° C (ΔT≈-7° C) – heating cycle at 4° C/min

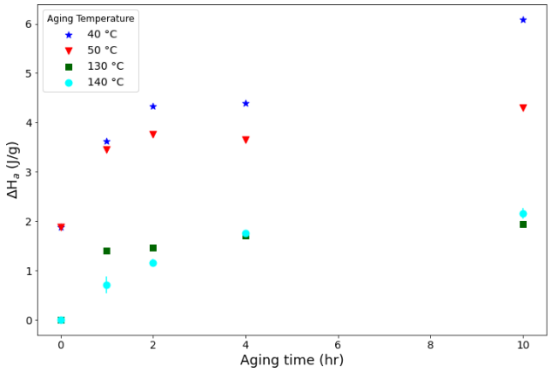

Figure 5- Enthalpy of aging of 8552 samples aged at different temperatures, as a function of aging time

4 conclusion

In this work, a characterization method for studying the physical aging behaviour of partially cured thermoset resins is proposed. Results of this work reveal that structure of the 3D network of a thermoset resin plays a significant role in its physical aging behaviour. Results of DSC experiments on partially cured Hexcel 8552 show that when a thermoset is in pre-gelation state, the effects of physical aging can be efficiently separated from the effects of residual cure reaction in enthalpy space. On the other hand, if the partially cured system advances to beyond gelation, the substantial overlap between physical aging and residual cure reaction mitigates accurate characterization of physical aging in partially cured thermoset resins. As a result, it is proposed that the result of characterization of physical aging in pre-gelation state, can be used to lay a foundation to debunk the overlap of physical aging and cure reaction in thermoset systems.

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