# Physical aging during cure of thermoset resin: effect of temperature

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## Introduction

The final properties of a thermoset matrix composite part are determined by the cure cycle used. A cure cycle typically consists of a constant rate ramp to one or more constant temperature holds. Faster heating rates take less time but lead to less uniform thermal distributions. Additionally, the isothermal hold can vary in temperature. For most epoxy matrices, the final hold temperature determines the maximum degree of cure (DoC) but often an intermediate hold temperature is used for various reasons, such as tooling material limitations.

The isothermal curing process of a thermoset resin is governed by the chemical reaction kinetics until vitrification, past which the rate of the cure reaction is controlled by diffusion phenomena. Current state-of-the-art cure kinetic models effectively account for both reaction kinetics and diffusion effects [1]. However, in the diffusion-controlled glassy state, the material properties tend to evolve towards thermodynamic equilibrium, a process referred to as physical aging. The change in the thermodynamic properties of the material with physical aging is illustrated in figure 1. Figure 2 demonstrates a commonly used cure cycle in the manufacturing of composite parts based on 8552 epoxy resin. As can be seen, the materials enters the glassy realm two hours in the curing process, and if kept in the hold for long periods, physical aging will progress and affect all subsequent properties, including residual cure behaviour and all mechanical properties including residual stress.

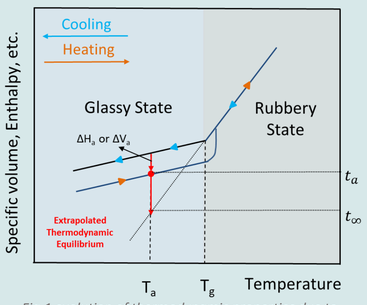


*Fig.1 evolution of thermodynamic properties due to physical aging at the aging temperature of $T_a$*

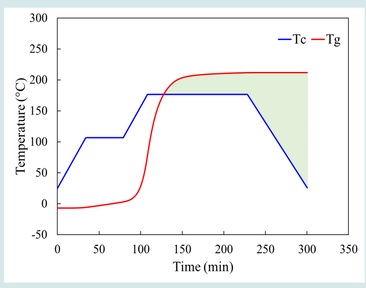


*Fig. 2 Manufacturer recommended cure cycle (MRCC) for Hexcel 8552 resin. Glass transition temperature ($T_g$) exceeds cure temperature ($T_C$).*

[1] Hubert, P., Johnston, A., Poursartip, A., & Nelson, K. "Cure Kinetics and Viscosity Models for Hexcel 8552 Epoxy Resin." *Proceedings of 29th International SAMPE Tech. Conf.* Long Beach, California, May 6-10, 2001. Society for the Advancement of Material and Process Engineering. Pp. 2341-2354

Currently, physical aging of thermosets during cure remains insufficiently understood and characterized, and is not included in existing material models. To address this gap, the systematic study of physical aging from the viewpoint of manufacturing of thermoset composite parts is required.

**In this work, physical aging during cure of a common thermoset resin used in the aerospace industry (Hexcel 8552) is methodically characterized, and the effect of different aging (cure) temperatures is investigated.**

*Image courtesy of TA Instruments*

## Methods

- Material system: Hexcel 8552 resin film
- Degassed at 60°C in vacuum oven for 2 hrs
- Cure kinetics model shows that cure advancement is negligible during this degassing [2]

**Temperature cycle: isothermal hold following by ramp to 270 °C at 2 °C/min**
Aging temperature ($T_a$) = 100 to 150 °C
Aging time ($t_a$) = 2 to 10 hours

- **Characterization method**: Temperature Modulated Differential Scanning calorimetry (TMDSC)
- inert gas ($N_2$) purge
- Modulation parameters: Period: 60s - Amplitude: ±1°C

[2] Shahkarami, A., Van Ee, D., & Poursartip, A. "Material Characterization for Processing: Hexcel 8552." *NCAMP (National Center for Advanced Materials Performance) 2009*

## Results

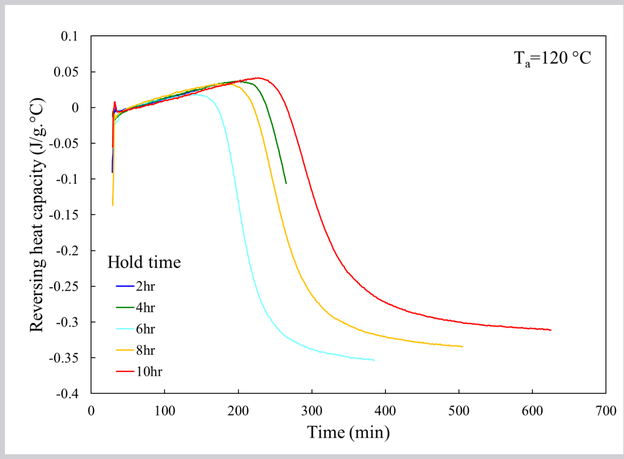


*Fig. 3 Reversing component of heat capacity of 8552 resin during an isothermal hold at 120 °C for different hold times*

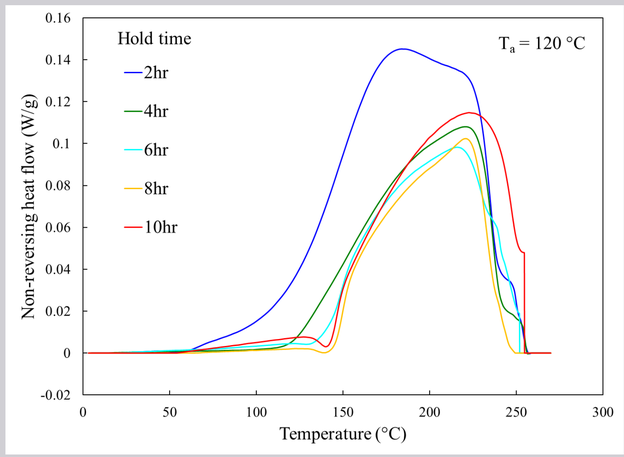


*Fig.4 DSC heat flow signal during the heating step to 270 °C at 2 °C/min , following the isothermal hold at 120 °C. Hold times vary between 2 to 10 hours.*

The evolution of the reversing heat capacity during an isothermal hold at 120 ° C is shown in Figure 3. The resin vitrifies after approximately 4 hours at this hold temperature, and physical aging is expected to develop past this time. The degree of cure for even the longest (10hr) hold is approximately 0.64, according to the model in [2].

When a residual heating ramp is applied to the specimens from Figure 3, an endothermic dip is observed prior to the exothermic peak that is associated with residual cure. This effect has been previously noted in the literature for curing materials but not systematically studied. The area under the endothermic peak increases with increasing hold time, consistent with the vast literature on cured epoxies [3].

Physical aging results in a delay in the re-initiation of the residual cure reaction during the heating ramp after the hold, and there is a progressive change in the shape of the residual heat flow with increasing hold time.

[3] Odegard, G.M., & Bandyopadhyay, A. "Physical Aging of Epoxy Polymers and Their Composites." *Journal of Polymer Science Part B: Polymer Physics* 49 (2011): 1695-1716

## Results

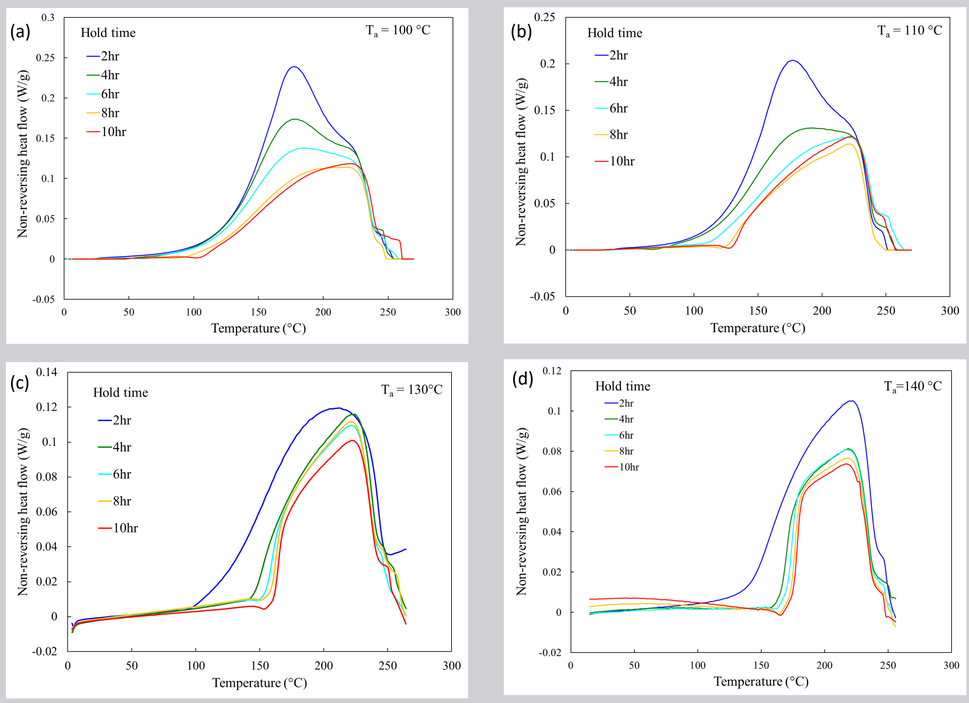


*Fig.5 DSC heat flow signal during the heating step to 270 °C at 2 °C/min following an isothermal hold at (a) 100 °C, (b) 110 °C, (c) 130 °C, and (d) 150 °C. Hold times vary between 2 to 10 hours.*

Figure 5 shows the non-reversing heat flow signal of 8552 resin at aging temperatures of 100 °C, 110 °C, 130 °C, and 150 °C respectively. The trends discussed in the previous section are consistent at the different aging temperatures: appearance of the endothermic peak with physical aging, increase in the magnitude of the endothermic peak with increase in hold time, and the change in the shape of the residual cure reaction exotherm with physical aging.

## Calculation of enthalpy of aging

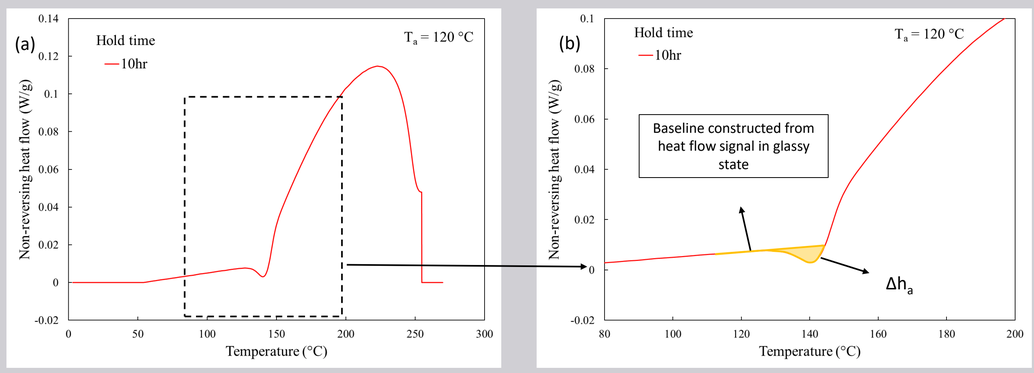


*Fig. 6 (a) heat flow signal of 8552 resin after 10 hours at 120 °C, during the heating step to 270 °C at 2 °C/min (b) zoomed view of fig. 6 (a): the area under the curve of the endothermic peak represents enthalpy of aging.*

The area of the endothermic peak is commonly used as a quantitative representation of the extent of aging, or aging enthalpy [3]. The common practice to obtain the aging enthalpy is to use the heat flow signal of a second heating ramp as the baseline for calculation of the area under the curve. However, most of the existing literature on physical aging covers thermoplastics and nominally fully cured thermosets, and this commonly used method cannot be used in the case of thermoset resin during cure. In this work, the baseline is constructed as a tangent line to the heat flow signal of the DSC test in the glassy range, as shown in figure 6(b).

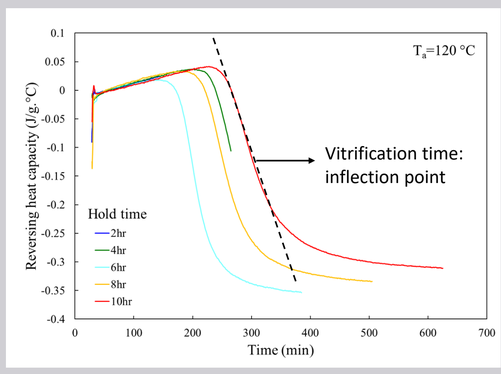


*Fig. 7 true aging times are calculated using the inflection point of the heat capacity step change*

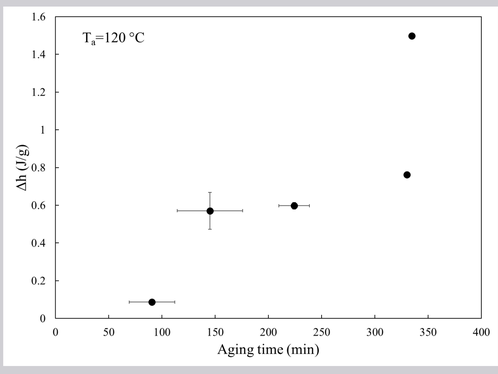


*Fig. 8 evolution of the enthalpy of aging as a function of aging time for 8552 resin held at 120 °C for different aging times*

The vitrification time of the resin samples held at 120 °C varies quite significantly (Figure 7). This can be attributed to the material's initial variability given the small DSC specimen size. The extraction of the true aging times is performed as follows: first, the vitrification time of the material is obtained via the inflection point of the glass transition step change in heat capacity signal. Then this value is subtracted from the time of the hold, which results in the time the material has spent in the glassy state, or true aging time.

Figure 8 is the cross-plot of the increase in aging enthalpy with true aging time for a hold temperature of 120 °C. Error bars are provided where test repeats were available. Although noisy and variable, the aging enthalpy is seen to measurably increase over timescales relevant to composites processing.

## Summary and future work

1. In this research, physical aging from the viewpoint of processing of carbon fiber reinforced thermoset polymers has been studied.
2. Systematic characterization of physical aging in thermoset resins during cure via DSC has been performed.
3. Aging enthalpy and true aging time are quantified, with the former requiring a modification to the methods used in the literature for thermoplastic polymers and nominally fully cured thermoset resins.
4. It is shown, in a quantifiable manner, that physical aging increases with aging time for a partially cured thermoset resin, and that this affects the residual cure behaviour.

**Future work:**
Development of a new experimental protocol to separate physical aging from the cure reaction, and investigation and further quantification of the behavior of physical aging of partially cured thermoset resins at different degrees of cure.