Assess volume changes associated with physical aging

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Abstract

Volume change associated with physical aging is measured for an epoxy resin (Diglydicidyl ether of bisphenol A (DGEBA, EPON-825)) using Differential Scanning Calorimetry (DSC), Thermomechanical Analysis (TMA) and a particular cure cycle. Results show a fingerprint of the volume variation, matching the endothermic peak, sign of physical aging effect observed in DSC.

About physical aging

Physical aging phenomenon corresponds to the enthalpy and volume relaxation happening during extended time periods at temperatures around the transition temperature T_g, during cure (crosslinking between polymer chains). It impacts mechanical properties fragilizing the resin and posing a challenge to industry (sustainability, safety, reliability). Physical aging effect can be erased by heating the resin at a temperature way above T_g, the **thermal rejuvenation [1]**.

Industry struggles to find models with physical aging behavior. This is why CRN and PH.D. Shaghayegh Kiafar try to characterize physical aging with enthalpy and volume and modify **DiBenedetto equation [2]** so that T_g also depends on physical aging.

$$T_g\ (\alpha) = T_{g0} + \frac{\alpha\lambda\ (T_{g\infty} - T_{g0})}{1-(1-\lambda)\alpha} = T_{g,tot}$$

Current DiBenedetto equation

→

$$T_{g,tot} = T_g\ (\alpha) + T_{g,Phys}(M)$$

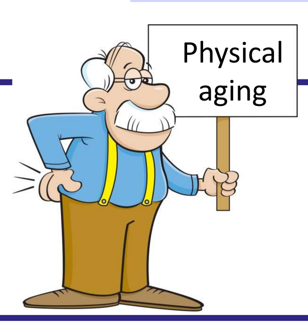
Research objective

With α the degree of cure, $\lambda = \frac{T_{g,0}}{T_{g,\infty}}$.

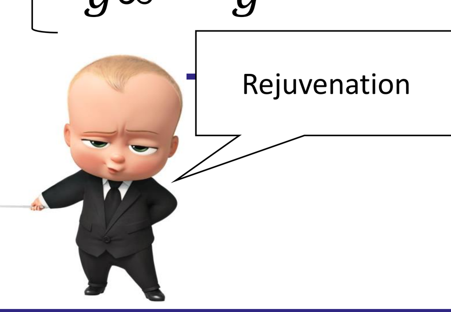
$T_{g0} = T_g$ when $\alpha = 0$

$T_{g\infty} = T_g$ when $\alpha = 1$

Objective



Study and characterize volume change due to physical aging



Materials and Method

Material system

DGEBA ($C_{21}H_{24}O_4$)

Base resins

+

DETA ($C_4H_{13}N_3$)

Curing agents

Cure cycle

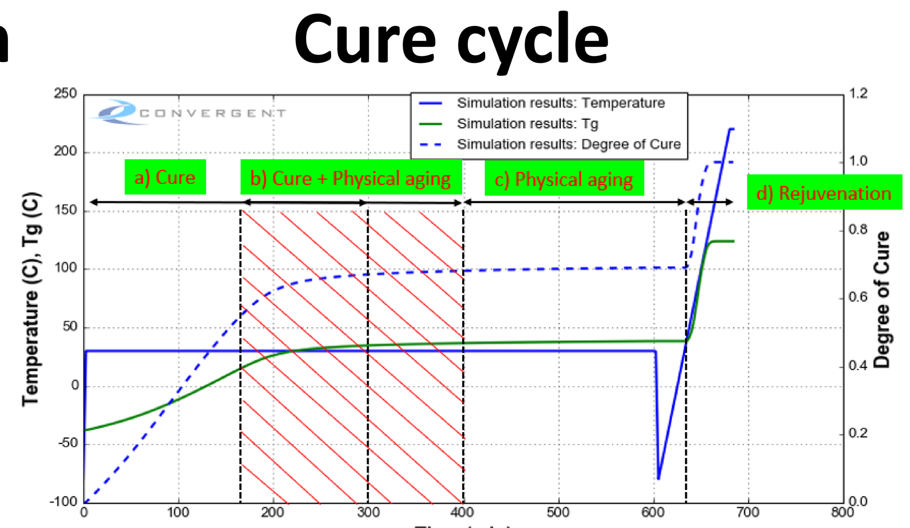


Figure 1: Temperature, transition temperature and degree of cure as a function of time. The blurry zone represents the area where physical aging starts.

DSC

- Resin and curing agent are mixed according to measured ratio.
- A drop is put in a hermetic pan for the chosen cure cycle.
- Modulations: 0.31°C for 30S.
- The isotherm time is varied .
- Results are analyzed on RAVEN (Convergent Manufacturing Technologies).
- Simulations are obtainable thanks to T. OKABE and coworkers [3].

TMA

Same mixture is put in a silicon mold with holes of 6mm diameter and 2cm depth. Then, the mold is put in an oven for 4 to 5h to cure. Samples are then tested in TMA with 0.01N load.

Figure 2: On the picture to the left, cured samples after 5 hours cure in the oven (transparent ones), and cures samples after being cut and tested in TMA. Silicon mold made and used for this study (right).

Results and Discussion

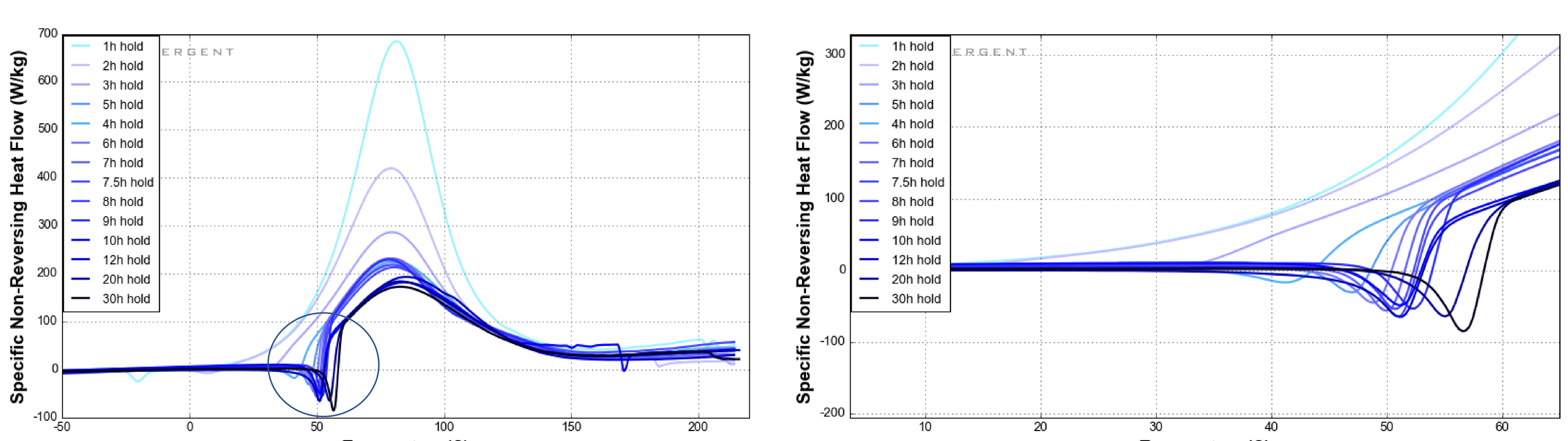


Figure 3: View of the heat flow exchange function of temperature during ramp segment after an isotherm at 30°C with different holding times. Figure on the right is a zoom of the circle containing the endothermic peaks (DSC results).

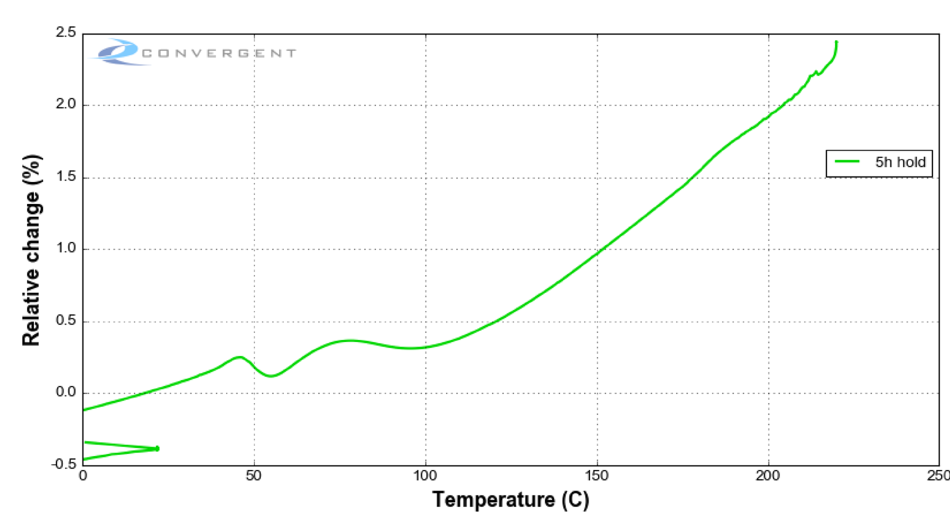


Figure 4: ***Relative change for a sample cured for 5 hours (TMA results).***

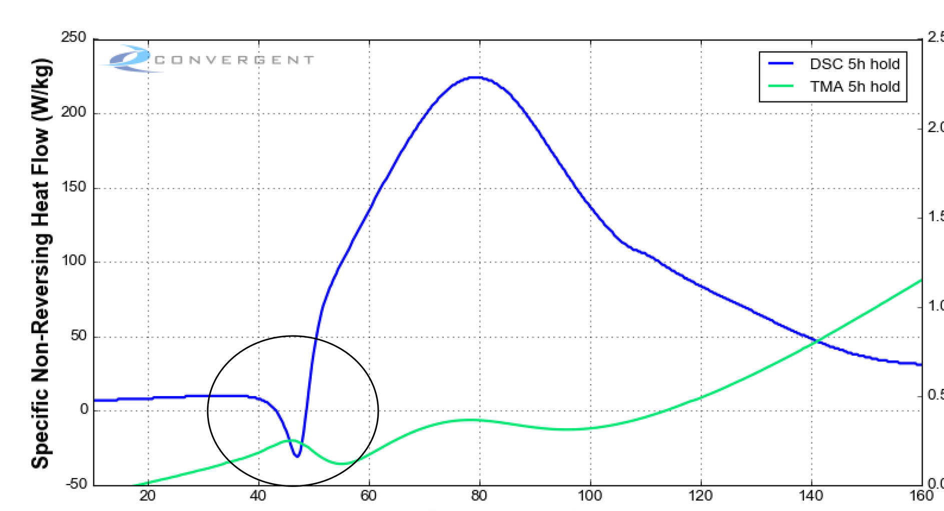


Figure 5: ***DSC and TMA comparison. The circle underline the endothermic peak (blue curve) and the volume expansion peak (green curve).***

- Endothermic peaks increase and shift to the right with longer hold time.
- A fingerprint of physical aging is observable in TMA (first green peak).
- Length and therefore volume expansion due to physical aging match perfectly the endothermic peak in DSC.

Conclusion

- Material system is ideal to observe how physical aging increases with hold time.
- TMA shows physical fingerprint, but measurements are not very precise.
- An optical dilatometer will be used for further experiments to improve results and help building a good model for physical aging.

References

[1] G. M. Odegard and A. Bandyopadhyay, "Physical aging of epoxy polymers and their composites," J. Polym. Sci. Part B Polym. Phys., vol. 49, no. 24, pp. 1695–1716, 2011.

[2] A. T. DiBenedetto, "Prediction of the glass transition temperature of polymers: A model based on the principle of corresponding states," Journal of Polymer Science Part B: Polymer Physics, vol. 25, no. 9. Journal of Polymer Science, Storrs, Connecticut, pp. 1949–1969, 1987.

[3] T. OKABE and P. D. . Co-Authors: Yuta Kumagai; Christophe Mobuchon, Ph.D.; Anoush Poursartip, Ph.D.; Yutaka Oya, "Molecular Dynamics Simulation to Predict Cure-Dependent Thermovolumetric Properties of Thermosetting Resin with Experimental Validation Corresponding." Submitted to Journal Polymer, 2020.