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Enthalpy Relaxation of a DGEBA Epoxy as a function of Time, Temperature, and Rate

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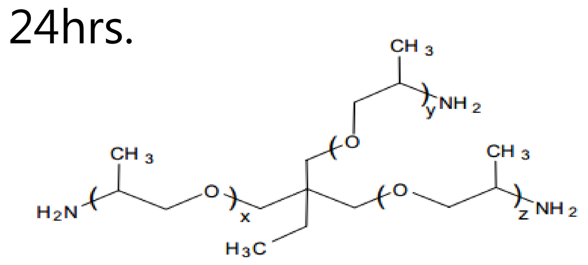
Abstract

Enthalpy relaxation resulting from physical aging of a DGEBA epoxy, Epon 828, cross-linked with an amine curative, Jeffamine T-403, was studied for two isothermal aging temperatures at sequential aging times up to two weeks. Results were analyzed using the peak shift method to obtain the relaxation parameters , ΔCp, Θ, and χ. The individual effects of cooling rate from the equilibrated state, aging time, and aging temperature were isolated to understand the initial state of the glassy epoxy and its evolution during physical aging.

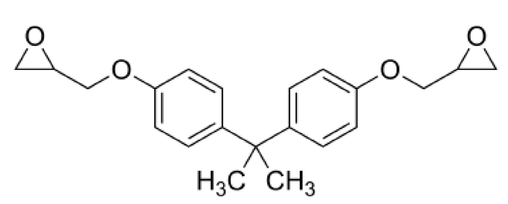
Background

828/T403

Momentive epoxy resin, Epon 828, was cured with a Huntsman polymetheramine, Jeffamine T-403 with a stoichiometric mix ratio of 100:43 ppw. Cured 80°C, 24hrs.



Jeffamine T-403



Diglycidyl ether of bisphenol-A (DGEBA)

Structural Relaxation

After a glass 'falls out' of equilibrium at the glass transition (T_g), the molecular mobility cannot compete with thermal contraction to rapidly minimize the free energy. Consequently, the timescale for the glass to reach equilibrium is enormous. At temperatures close to, but below the T_g this process is shifted to experimentally observable timescales and structural recovery (relaxation) can be measured upon reheating the glass through T_g. The resulting peak is referred to as enthalpy relaxation.

KAHR Model

A constitutive model proposed by Kovacs, Alkonis, Hutchinson, and Ramos (KARH) has been successful in predicting relaxation phenomena in the realm of T_g.

$$\frac{d\delta_H}{dT} = -\Delta C_p - \frac{\delta_H}{\tau q}$$

Where the relaxation time, τ, is expressed as the following:

Temperature Dependence

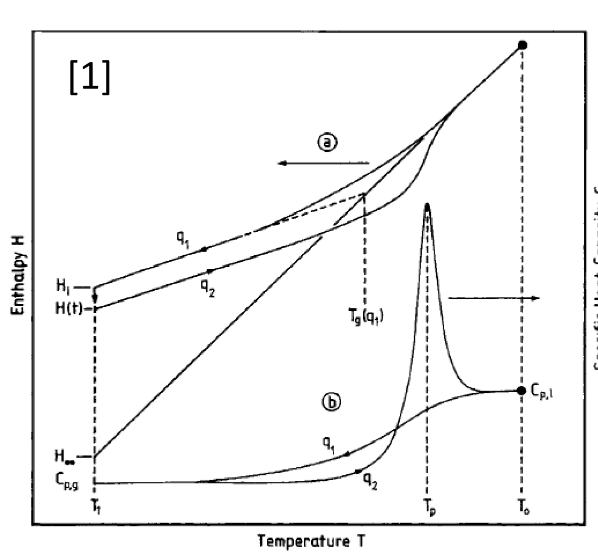
$$\tau = \tau_i \exp[\Theta(T_r - T)] \exp[-(1-\chi)\Theta\delta/\Delta C_p]$$

Structure Dependence

Where χ, a partition parameter, and Θ, the KAHR parameter, are both material constants between 0 and 1.

$\overline{\delta_H}$=Hi-H(t)

$\delta_H(t)$=H(t)-H_∞



Experiment

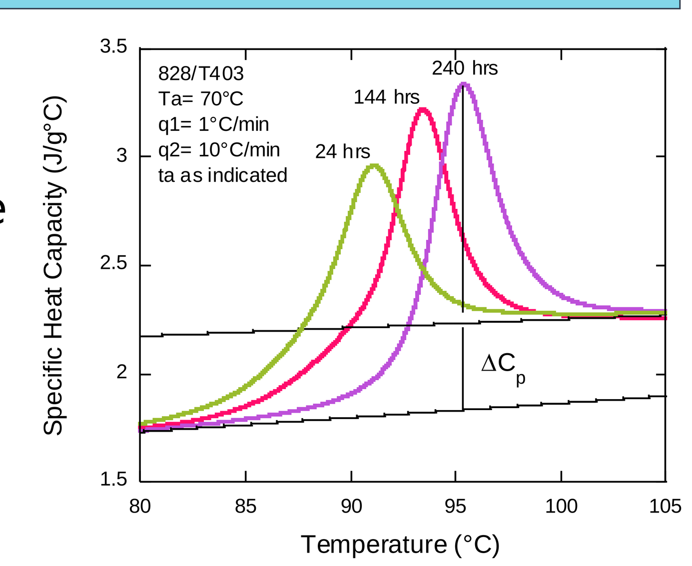
Utilizing a TA Q2000 differential scanning calorimeter, the subsequent isothermal experiments were ran on 828/T403. 10-15mg hermetically sealed DSC samples were prepared and subjected to a number of unique thermal histories described by the variables in Table 1. Where possible, experiments were ran exclusively in the DSC chamber. Specific thermal history is indicated on the graph.

Variables	Values
Isothermal Aging Temperature, Ta (°C)	70, 78
Isothermal aging time, ta (hrs)	3, 24, 72, 144, 240
Cooling rate, q1 (°C/min)	0.2, 1, 2.5, 5, 10, 15, 20
Heating Rate, q2 (°C/min)	1, 2.5, 5, 10, 15, 20

The following is an analysis of the resulting parameters: **ΔCp, Θ, and χ** primarily through examination of the peak temperature, T_p, dependence.

Evaluation of ΔCp

The change in heat capacity between the 'liquid like' rubbery state and glassy state was measured from heating cycles for all thermal histories considered.



$\Delta C_p = (C_{pl} - C_{pg})_{Tp}$ = 0.435 +/- 0.028 J/g°C

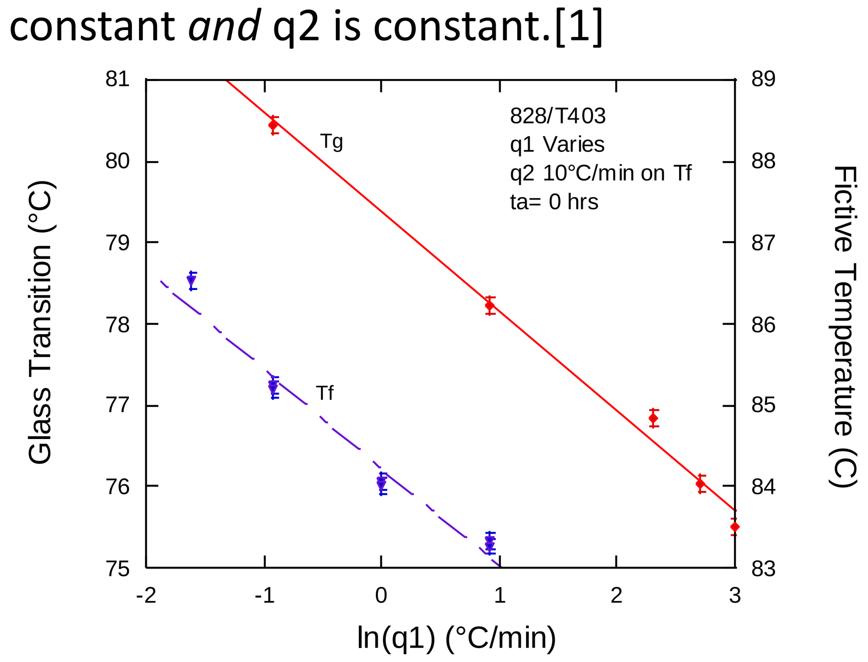
Evaluation of ϴ

The KAHR parameter, ϴ, can be found from a number of relationships. The glass transition temperature is function of only one experimental variable, cooling rate, and the following expression can be derived :

$$\left(\frac{dT_g}{d\ln|q1|}\right)_{T_0 \gg T_g} = \Theta^{-1}$$

ϴ(T_g)= (1.219)$^{-1}$=0.820K^{-1}
ϴ(T_f)= (1.214)$^{-1}$= 0.824 K^{-1}

Likewise, the dependence of fictive temperature, Tf can be expressed through the similar relationship when the thermal history is constant *and* q2 is constant.[1]



Evaluation of χ

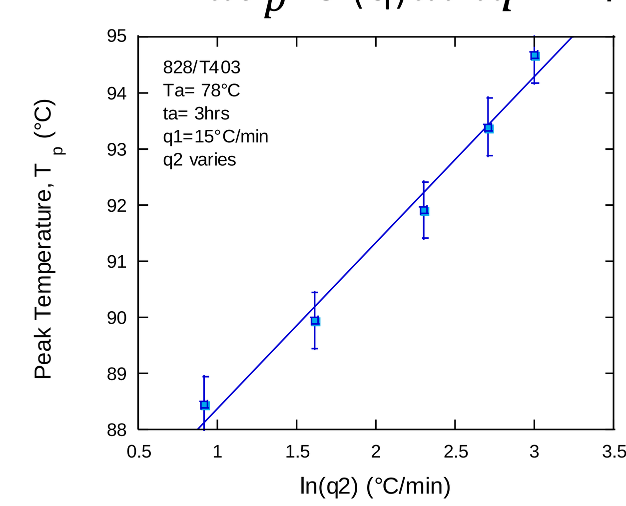
T_p can be expressed as the sum of the partial derivatives of T_p with respecting to heating rate, thermal history, and isothermal aging temperature where cooling rate and isothermal aging time are buried in δ_H.

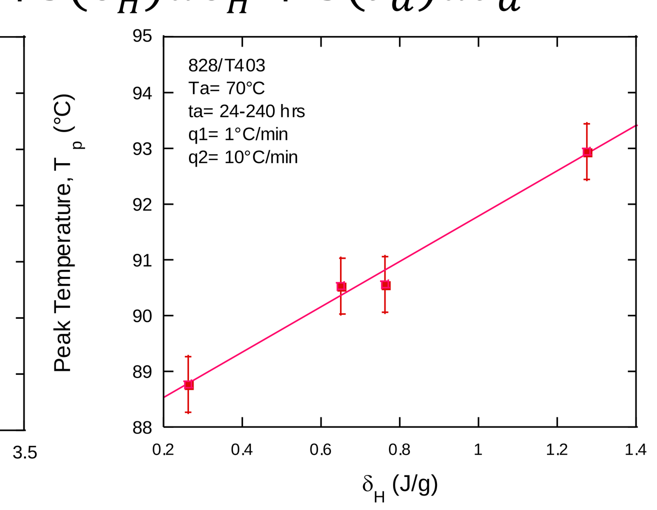
$$d\mathcal{T}_p = \left(\frac{d\mathcal{T}_p}{d\ln q}\right) d\ln q + \left(\frac{d\mathcal{T}_p}{d\delta_H}\right) d\delta_H + \left(\frac{d\mathcal{T}_p}{d\mathcal{T}_a}\right) d\mathcal{T}_a$$

Substitution of the following reduced variables gives rise to the shift factors for heating rate, $\hat{s}(Q2)$, and isothermal recovery, $\hat{s}(\overline{D})$ in terms of experimental variables.

$\mathcal{T}$=ϴT   Q2= ϴq $\overline{D} = \frac{\Theta\delta_H}{\Delta C_p}$

$$d\mathcal{T}_p = \hat{s}(q) d\ln q = +\hat{s}(\delta_H) d\delta_H + \hat{s}(\mathcal{T}_a) d\mathcal{T}_a$$





Determination of the heating rate shift factor and isothermal recovery shift factor result from the slopes of the above curves.

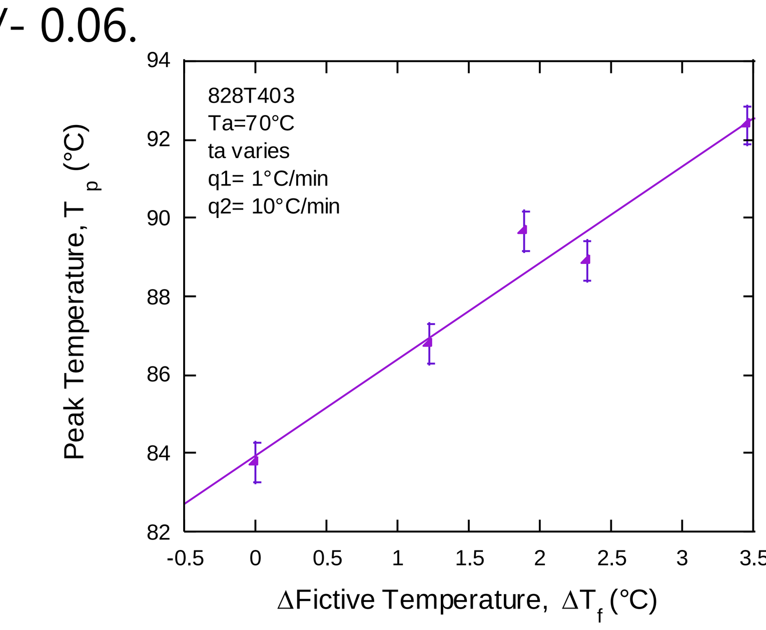
$$\hat{s}(Q2) = \Theta\left(\frac{dT_p}{d\ln q2}\right)_{q1,\overline{\delta_H},T_a}$$ **0.822*2.963=2.44**

$$\hat{s}(\overline{D}) = \Delta C_p\left(\frac{dT_p}{d\ln q}\right)_{q1,q2,T_a}$$ **(0.435)*4.070= 1.77**

A reasonable approximation of χ can be made from:

$$\hat{s}(Q2) - 1 \cong \hat{s}(\overline{D}) \cong \chi^{-1} - 1$$

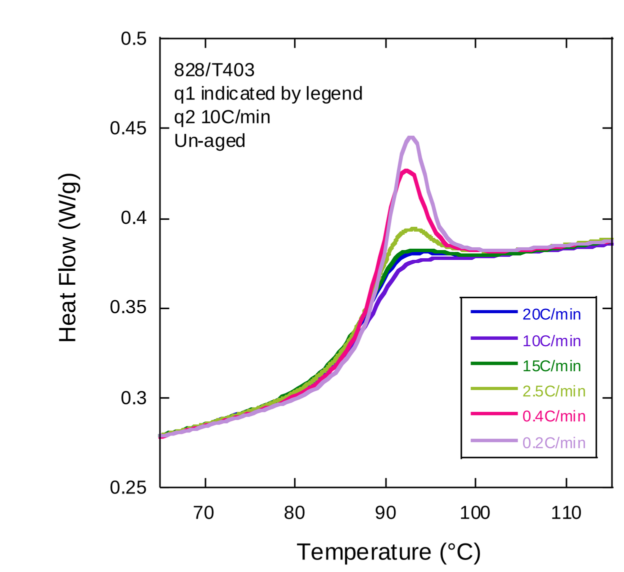
This places χ at 0.41 +/- 0.03 and 0.36 +/- 0.02. Hutchinson *et al.* showed that $\hat{s}(Q2) - 1$ is seen to be less than $\hat{s}(\overline{D})$ (the case here) [2, 3]. The difference is comparable to reported values [2, 4, 5]. A last check is to plot T_p vs. ΔT_f as suggested by others [3, 4]. The slope should yield a comparable value of χ, which it does. χ= 0.40 +/- 0.06.

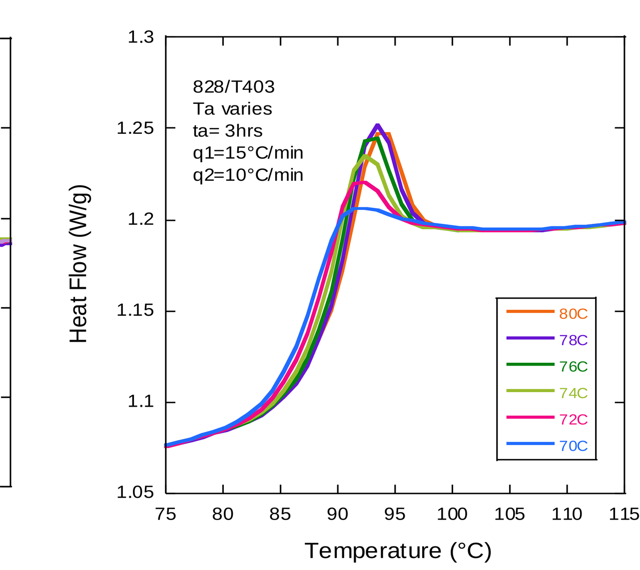


Conclusions and Future Work

Use of the peak shift method has provided reasonable values for the relaxation parameters, ΔC_p, ϴ, and χ. Marginal differences were observed between the two experiments determining χ and confidence reaffirmed by the T_p vs. ΔT_f from evaluation of the enthalpy curves, $\delta_{H(t)}$ for the 70°C, long term aging experiments. Isothermal aging was performed at T_g-2°C and T_g-10°C for constant, short time (3 hrs.) in the case of one and a range of times in the case of the other (24-240 hrs.) These thermal histories represent two sides of the spectrum, but perhaps additional testing well below Tg is needed to confirm that the glass is both well-stabilized, and the relaxation parameters accurate.

The true test of the peak shift method is to use the values, alongside the model, to predict the experimental results used to parametrize the model and other results such as the temperature, cooling rate, or time dependence.





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