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# Physical Aging of an Epoxy Resin for Civil Engineering Applications from Fast Scanning Calorimetry Investigations

Blandine Queleennec, Nicolas Delpouve,\* Laurent Delbreilh, Romain Delannoy, and Emmanuel Richaud

This work deals with the structural relaxation of an epoxy resin based on bisphenol A diglycidyl ether polymer (DGEBA) and 4,7,10-Trioxa-1,13-tridecanediamine (TTDA) hardener. The physical aging experiments are performed in situ using fast scanning calorimetry (FSC). The profile of the relaxation enthalpy with temperature is obtained close to the glass transition by annealing the resin during 10 min at various aging temperatures. From this profile, the structural relaxation is probed at various distances from the glass transition temperature, with aging times ranging from 0 to 1000 min. The Tool–Narayanaswamy–Moynihan (TNM) model is employed to analyze the relaxation data.

## 1. Introduction

Epoxy resin addition in concrete structures is of primary interest to stop water infiltration. These constructions are targeting 100 years applications but nowadays there is no definitive way to predict the behavior of an epoxy resin at such a long-time scale, even less the possible interactions between the different aging processes. Indeed, epoxies are sensitive to water uptake, thermo-oxidation, and structural relaxation, the latter being the focus of the present work. During the structural relaxation, or physical aging, the out-of-equilibrium glass minimizes its thermodynamic quantities, such as enthalpy and specific volume, to approach equilibrium. In glassy polymers, this phenomenon can negatively affect the dimensional stability during storage,

resulting in the degradation of mechanical and barrier properties, as examples. It can be quantified from the calculation of the enthalpy of recovery thanks to calorimetric measurements.

The emergence of fast scanning calorimetry (FSC) has raised the interest of researchers for the investigation of physical aging in various systems. During an FSC experiment, a sample with a low mass (about tens to hundreds nanograms) is heated up and cooled down at rates in the order of thousand Kelvins per second. FSC can generate glassy polymers with high level of enthalpy or specific volume.<sup>[1]</sup> Moreover, since the glass transition is shifted to

higher temperatures when increasing the cooling rate, the physical aging can also be investigated at temperatures higher than in standard differential scanning calorimetry. Besides, the structural relaxation can be tracked in accelerated conditions since the ratio surface/volume is significantly increased.<sup>[2]</sup> Therefore, the physical aging is easier to follow in its entirety. The goal of this study is thus to take benefit of the FSC to investigate the features of the structural relaxation in an epoxy polymer considered for civil engineering applications.

## 2. Results and Discussion

Figure 1a shows the FSC response, that is, the heat flow normalized to the sample mass and the heating rate, consecutive to aging procedures for 10 min at temperatures ranging from 80 to 40°C. One can observe first an increase of the enthalpy of recovery, which manifests by an endothermic peak superimposed to the glass transition heat flow step, when decreasing the aging temperature  $T_{ag}$ . Close to the glass transition, the values of the enthalpy of recovery are in agreement with the line defined by  $\Delta H_{\infty} = \Delta C_p * (T_{gmid} - T_{ag})$ , where  $\Delta H_{\infty}$  is the total enthalpy loss, defined as the change needed in the enthalpy of recovery to reach the thermodynamic equilibrium. By decreasing  $T_{ag}$ , the data progressively diverge from this line, showing that the equilibrium has not been reached yet. When aging farther from the glass transition, the enthalpy of recovery starts decreasing, which is consistent with the progressive reducing of the molecular mobility. The result is the enthalpy profile given in Figure 1b.

In a second step, the aging kinetics were investigated at various temperatures. In Figure 2a, the FSC curves are given, following

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B. Queleennec, N. Delpouve, L. Delbreilh  
Normandie Univ  
UNIROUEN Normandie  
INSA  
Rouen, CNRS  
Groupe de Physique des Matériaux  
St Etienne du Rouvray  
Paris 76800, France  
E-mail: nicolas.delpouve1@univ-rouen.fr  
R. Delannoy, E. Richaud  
PIMM  
CNAM  
CNRS UMR 8006  
Arts et Métiers–ParisTech  
151 bd de l'Hôpital  
Paris 75013, France

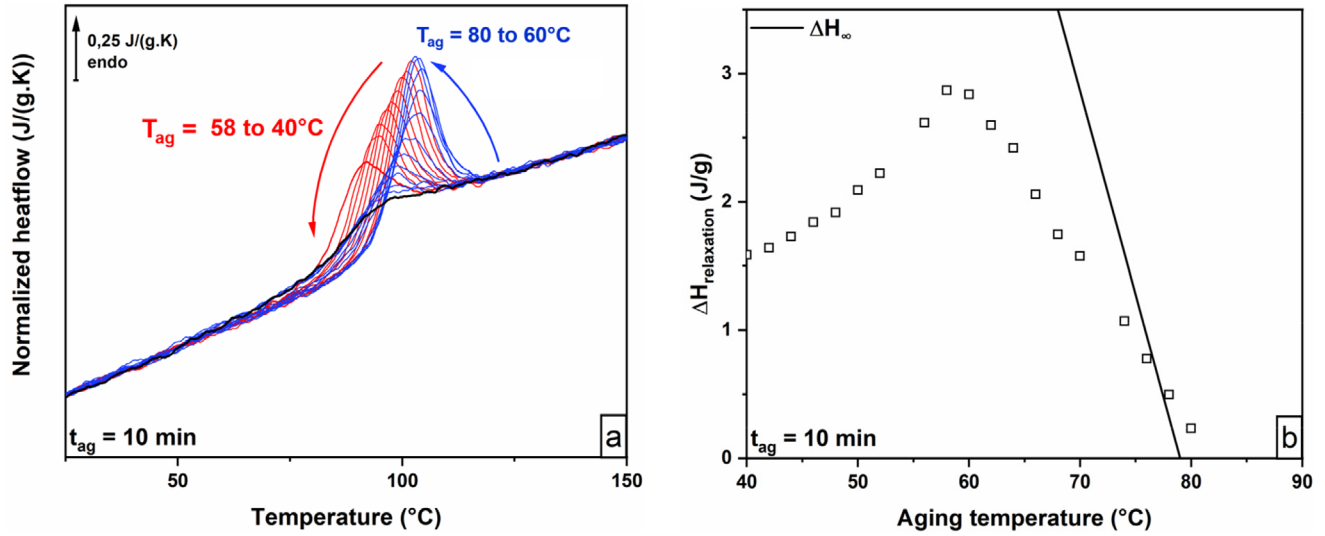


Figure 1. a) Fast scanning calorimetry (FSC) curves following an annealing for 10 min at aging temperatures ranging between 40 and 80°C. b) Enthalpy of recovery as function of the aging temperature for 10 min aging. The solid line indicates how evolves the total enthalpy loss with the aging temperature.

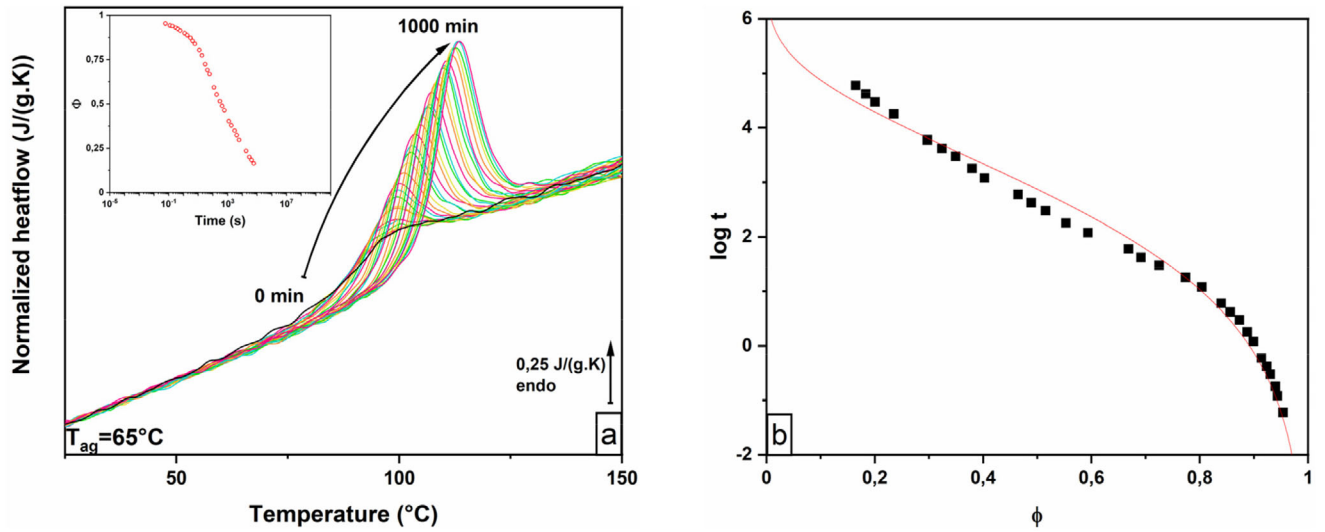


Figure 2. a) FSC curves following an aging at  $T_{ag} = 65^\circ\text{C}$  for aging times ranging between 0 and 1000 min. The resulting relaxation function is given in inset. b) Application of TNM model for  $T_{ag} = 65^\circ\text{C}$ . FSC, fast scanning calorimetry; TNM, Tool–Narayanaswamy–Moynihan.

the aging at  $T_{ag} = 65^\circ\text{C}$  from 0 to 1000 min. In the inset the relaxation function  $\phi$  plotted from equation (Equation 1) is added.

$$\phi = \frac{\Delta H_{\infty} - \Delta H_{relaxation}}{\Delta H_{\infty}} \quad (1)$$

Then, when the amount of data was sufficient, which is the case for temperatures slightly below the glass transition, the Tool–Narayanaswamy–Moynihan (TNM) model has been applied (Equation 2).

$$\tau = A * e \left( \frac{\Delta h^* x}{R * T_{ag}} + \frac{\Delta h^* (1-x)}{R * T_f} \right) \quad (2)$$

By substitution in the KWW function (Equation 3), this leads to (Equation 4) from which Figure 2b is plotted.

$$\phi = e - \left( \frac{t}{\tau} \right)^{\beta_{KWW}} \quad (3)$$

$$t = (Ln\phi)^{\frac{-1}{\beta_{KWW}}} * (-A) * e^{\left( \frac{\Delta h^* x}{R * T_{ag}} + \frac{\Delta h^* (1-x)}{R * T_f} \right)} \quad (4)$$

where  $\tau$  is the relaxation time,  $\beta_{KWW}$  the stretching exponent,  $A$  the pre-exponential factor,  $x$  the nonlinearity parameter,  $\Delta h^*$  the activation energy, and  $T_f$  is the fictive temperature, defining the temperature at which any property, related to the structural relaxation, is at equilibrium. The best fits obtained for  $T_{ag} = 65^\circ\text{C}$  and  $50^\circ\text{C}$  provide values of  $\beta_{KWW}$  close to 0.5, and are consistent with the equation  $x = (\beta_{KWW} - 0.2)/1.05$ , as proposed by Hodge<sup>[3]</sup> (see Table 1).

**Table 1.** Structural relaxation Tool–Narayanaswamy–Moynihan (TNM) parameters at  $T_{\text{ag}} = 50^\circ\text{C}$  and  $65^\circ\text{C}$ .

	$\Delta h^*$ [kJ mol <sup>-1</sup> ]	$\beta_{\text{KWW}}$	$x$
$T_{\text{ag}} = 50^\circ\text{C}$	638	0.45	0.24
$T_{\text{ag}} = 65^\circ\text{C}$	668	0.50	0.29

### 3. Conclusion

FSC results have been depicted by the TNM model close to the glass transition temperature. The stretching exponent agrees with values generally reported for epoxy resins. Further investigations will probe the relaxation at lower temperatures and under degrading environments in order to offer quantitative data that could be useful for civil engineers.

### 4. Experimental Section

The epoxy system was obtained from the epoxy prepolymer DGEBA, cured with 4,7,10-Trioxa-1,13-tridecanediamine (TTDA), in stoichiometric proportions. After mixing, the blend was set to solidify for 3 h in closed vials to avoid any potential hardener evaporation. Epoxy film was then manufactured using a heating hydropress for 1 h at  $50^\circ\text{C}$ , and 1 h at  $90^\circ\text{C}$ , and finally post-cured at  $170^\circ\text{C}$  under vacuum until obtaining a 100% cured network.

FSC experiments were performed thanks to a Mettler Toledo Flash DSC 1 apparatus, which was connected with a Huber TC100 intra-cooler that allowed the cooling of samples down to  $-90^\circ\text{C}$  and heating/cooling scans at rates up to  $4000\text{ K s}^{-1}$ .<sup>[4]</sup> Before any experiment, the calibration procedures recommended by the purchaser, that is, the corrections steps as well as the conditioning, were ensured. The cell was swept by gaseous nitrogen at  $20\text{ mL min}^{-1}$  during each experiment. The sample was positioned in the middle of the chip sensor to optimize the thermal contact. Static and dynamic thermal lags were corrected with the help of an indium standard, and by repeating heating and cooling scans at the same rate, respectively.<sup>[4]</sup> The sample mass, about 25 mg, was determined by assuming equality between the heat capacity step  $\Delta C_p$  obtained from the glass transition in MT–DSC (Q2000 Thermal Analysis) and in FSC on an epoxy resin. Physical aging was carried with the following procedure: the sam-

ple was heated up to  $200^\circ\text{C}$  and held 0.1 s to erase any previous thermal history. Then, the sample was cooled down to the aging temperature  $T_{\text{ag}}$ , aged isothermally for aging times  $t_{\text{ag}}$ , and finally cooled down to  $-70^\circ\text{C}$ . Subsequently, the sample was heated to  $200^\circ\text{C}$ . All heating and cooling scans were performed at  $1500\text{ K s}^{-1}$ .

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

Research data are not shared.

### Keywords

epoxy polymer, flash DSC, glass transition, structural relaxation, TNM model

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