

# THERMAL, RHEOLOGICAL AND MECHANICAL PROPERTIES OF EPOXY RESIN FORMULATIONS

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## Abstract

This study aimed at identifying the most suitable combination of epoxy and hardener for filament winding composite manufacturing. The curing behavior of formulations prepared with a combination of epoxy resins (called E1 and E2) and hardeners (called H1 and H2) were investigated by non-isothermal differential scanning calorimeter analysis, rheometry, and Fourier-transform infrared (FTIR) spectroscopy. Post-cured formulations were also characterized using thermal (DMA, TGA) and mechanical (tensile strength) analyses. The E2 resin formulations showed higher glass transition temperature, higher storage modulus, and thermal stability. In addition, the viscosity of E1 and E2 at 60 °C were similar. Higher storage modulus results were found for the E2H1 sample, although both E2H1 and E2H2 showed similar glass transition temperatures. In all, the E2H1 formulation showed the most suitable overall performance.

**Keywords:** Epoxy, rheology, thermal analysis, glass transition temperature.

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## Introduction

Epoxy resins are thermosetting polymers usually obtained by reacting epichlorohydrin with bisphenol, and characterized by two or more epoxy groups per molecule through which the crosslinking reaction (curing) takes place. The final polymer properties depend on the hardener, the curing conditions, and the degree of conversion achieved [1]. The hardener determines the mechanism of the curing reaction and consequently influences the curing kinetics, the processing cycle (viscosity as a function of time), and the gelation and properties of the cured material [2, 3]. Examples of hardeners for epoxy resins are: amines, amides, anhydrides, imidazoles, boron trifluoride complexes, phenols, and metallic oxides [4,5].

Due to their excellent thermal and mechanical properties, epoxy resins stand out due to their various applications such as: coatings, paints, and composite materials. Several processes work with epoxy for manufacturing composite materials [1], including filament winding, where performance, material qualification, and product consistency are paramount requirements for aerospace components, pipes, tubes etc. Many thermosets applied in composites are cured using complex cure cycles to optimize the tradeoff between processing time and final product properties. Thus, understanding the viscoelastic properties of a thermoset resin is essential. It is also vital to monitor viscosity, gel temperature, onset and peak curing temperature, degree of curing, and glass transition temperature to optimize the manufacturing [6].

This study aimed at identifying the most suitable combination of epoxy and hardener for filament winding composite manufacturing. The curing behavior of formulations prepared with a combination

of epoxy resins (called E1 and E2) and hardeners (called H1 and H2) were investigated, along with various analyses of the cured resin systems.

## Experimental

### Materials

Two diglycidyl ether of bisphenol A (DGEBA)-based epoxy resins, called E1 and E2, with viscosity at 25 °C (ISO 3219) of 1300-1500 and 7000-10000 mPa.s, respectively, and two anhydride-based hardeners, called H1 and H2, with viscosity at 25 °C (ISO 3219) of 90-100 and 150-300 mPa.s, respectively, were studied. All materials were donated by Olin Corporation.

### Methods

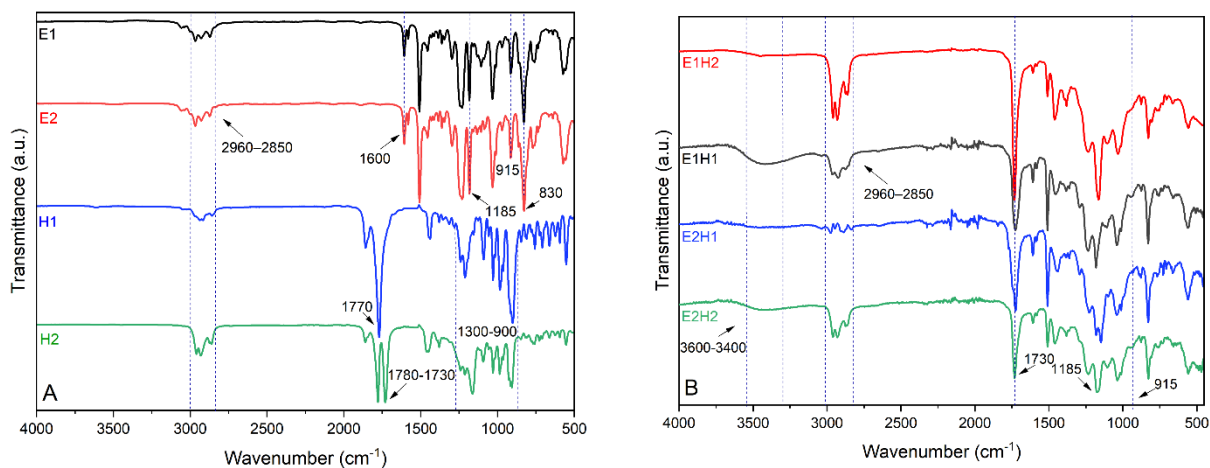
Four different formulations were produced with the available materials, named E1H1, E1H2, E2H1, and E2H2. For example, E1H1 sample was prepared with epoxy E1 and hardener H1. The epoxy:hardener ratio was 1:1. Samples for DSC and rheometry were prepared by mixing epoxy and hardener just prior to the analysis. The other samples were prepared by casting the mixture into a silicon mold, and curing in an oven for 24 h at 60 °C, followed by post-curing for 1-2 h at 90 °C and 4-6 h at 140 °C as per the manufacturer datasheet.

Rheological analysis (Anton Par rheometer, MCR 101) was carried out at 60 °C in the shear-rate of  $1 \text{ Hz}\cdot\text{s}^{-1}$ , at a rotation speed of 60 rpm (ASTM D2983), with a cone-plate geometry. In the rheological analysis, the viscosity at 60 °C was measured and the gel time was taken as that corresponding to the change in slope of the two linear parts of the curve. Fourier-transform infrared spectroscopy (FTIR) was performed using the ATR technique in a Perkin Elmer, Spectrum 1000 in the  $450\text{-}4000 \text{ cm}^{-1}$  range. For each sample (neat resins, neat hardeners, and post-cured formulations), 32 scans were recorded with a resolution of  $4 \text{ cm}^{-1}$ . Differential scanning calorimetry (DSC) analysis was conducted in a TA Instruments Q20 calorimeter under a nitrogen atmosphere with a flow-rate of  $50 \text{ mL}\cdot\text{min}^{-1}$ . Each formulation ( $\sim 10 \text{ mg}$ ) was subjected to the following cycle: heating from room temperature to 200 °C (to measure enthalpy of curing), cooling to 25 °C, and heating to 200 °C (to measure the  $T_g$  of the cured sample). All heating and cooling rates were of  $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ . Dynamic-mechanical analysis (DMA) was performed in a TA Instruments TA2980 equipment using dual cantilever mode, dimensions of  $(35 \times 12.6 \times 4) \text{ mm}$ , with a frequency of 1 Hz and  $4.4 \text{ }\mu\text{m}$  (linear viscoelastic region) of amplitude, using a heating rate of  $1 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ , from room temperature to 250 °C. Thermogravimetric analysis (TGA) was performed in a TA Instruments Q50 equipment on the post-cured samples ( $\sim 10 \text{ mg}$ ), under nitrogen gas flow ( $50 \text{ mL}\cdot\text{min}^{-1}$ ), at a heating rate of  $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ , from room temperature to 900 °C.

## Results and Discussion

Fig. 1 shows the FTIR results for neat resins, hardeners and post-cured formulations. In Fig. 1A, in both resins (E1 and E2), it is possible to verify the presence of oxirane groups ( $915 \text{ cm}^{-1}$ ), the ether group ( $1185 \text{ cm}^{-1}$ ), alkane group (between  $2960\text{-}2850 \text{ cm}^{-1}$ ), and C=C bonds in aromatic rings ( $1600$  and  $830 \text{ cm}^{-1}$ ). It is also possible to verify for the hardeners bands of different intensities within  $1730\text{-}1780 \text{ cm}^{-1}$  referring to the C=O group, as well as in the  $1300\text{-}900 \text{ cm}^{-1}$  region referring to the C-O group.

Fig. 1B presents the FTIR spectra of the post-cured formulations. The non-appearance of band  $915 \text{ cm}^{-1}$  indicates complete cure. The attenuation of the C=O band of the carboxylic groups ( $1720\text{-}1700 \text{ cm}^{-1}$ ) indicates that the crosslinking reactions occurred, as well as the band at  $1180 \text{ cm}^{-1}$  of the C-O bonds in the chain [7,8].



**Figure 1.** FTIR spectra of neat resins and hardeners (A) and the post-cured formulations (B).

Table 1 summarizes the data from DSC relative to peak temperature ( $T_{\text{peak}}$ ), enthalpy of curing ( $\Delta H$ ), and the glass transition temperature ( $T_g$ ). In all formulations, an exothermic peak was found around 143 °C, indicating similar crosslinking reactions [8]. However, the enthalpy varied, with the highest value (219 J/g) found for the E1H2 sample, indicating a greater release of energy in the curing reaction. This agrees with the FTIR results, which presented a weaker band in the region of the oxirene group (915  $\text{cm}^{-1}$ ). The  $T_g$  results from the second heating scan occurred within 90-110 °C. The E2H2 formulation showed higher  $T_g$  (110 °C), indicating greater mobility resistance of the polymeric chains in the rubbery state [9].

**Table 1.** DSC, DMA and TGA results for the studied formulations.

Sample	$T_{\text{peak}}$ (°C) (DSC)	$\Delta H$ (J/g) (DSC)	$T_g$ (°C)		$T_{\text{peak}}$ (°C) (loss modulus)	$E'_g$ @50 °C (MPa)	$E'_r$ @140 °C (MPa)	$E''$ @25 °C (MPa)	$T_{10\%}$ (°C) (TGA)
			DSC	DMA (tan delta)					
E1H1	143	167	90	105	67	1190	1.6	118	320
E1H2	143	219	100	106	67	1307	4.2	118	390
E1H1	143	205	95	119	88	1506	4.8	145	350
E2H2	142	186	110	119	77	939	2.5	73	380

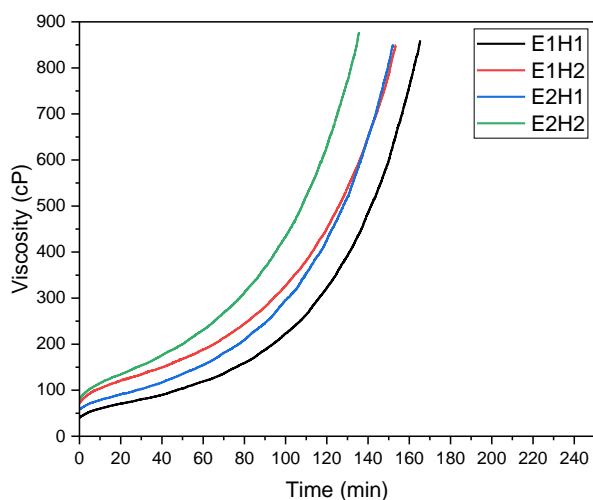
The  $T_g$  was also determined from the the tan delta data of the DMA analysis, and it is shown in Table 1 along with the storage modulus in the glassy ( $E'_g$ ) and in the rubbery ( $E'_r$ ) region, and the loss modulus ( $E''$ ) at 25 °C. The E2H1 formulation obtained higher  $E'$  in the glassy and rubbery regions, indicating greater crosslinking, constituting a three-dimensional network, and higher  $T_g$ . Some difference in the  $T_g$  results from DSC and DMA analyses is seen because each analysis is sensitive to a specific region, and the DSC analysis has a lower sensitivity in the glassy region, compared with DMA, making DMA more accurate for  $T_g$  determination.

From TGA analyses of the post-cured formulations, similar mass loss behavior can be observed, and the onset of thermal decomposition occurred at ~250 °C, with mass losses ranging from 3% to 5% for all samples. Degradation occurs in one step, with the maximum weight loss temperature at ~ 420 °C. However, the temperature for 10% mass loss ( $T_{10\%}$ ), shown in Table 1, varied for the samples. The H2 hardener, compared to H1, increased the thermal stability of the formulations, and the E1H2 sample presented better thermal stability based on the  $T_{10\%}$ .

Fig. 2 displays viscosity curves over time. The resin system E2H2 exhibits a more pronounced viscosity increase, while the E1H2 and E2H1 systems show similar behavior, and E1H1 took longer to show a significant increase. The initial viscosity rise is associated with chain size and growth. Due to its higher molar mass, the E2 resin displays greater viscosity changes in the early stages [4]. The

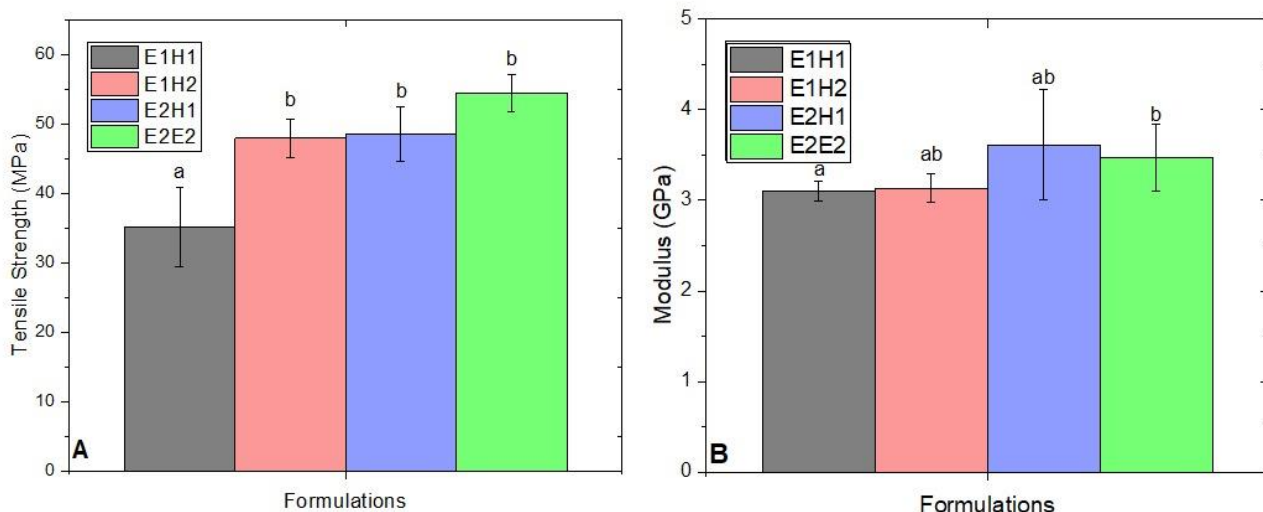
viscosity increase after a specific temperature is associated with the early crosslinking stages (formation of the three-dimensional network). All resins showed overall similar behavior, and the lowest viscosity was found for E1H1 formulation.

The estimated gel time was 120, 110, 109, and 90 min for E1H1, E1H2, E2H1, E2H2 systems, respectively. The longer the gel time, the longer the processing window at this temperature.



**Figure 2.** Curing progression in terms of viscosity vs time for the studied formulations at 60 °C.

Fig. 3 shows the tensile strength and modulus results for the studied formulations. For the tensile strength, the highest mean value was found for the E2H2, and the lowest for the E1H1 sample, while E1H2 and E2H1 showed similar results. As for modulus, the E2H1 and E2H2 showed higher mean values, with a significant difference found for the E2H1 sample only.



**Figure 3.** Tensile strength and modulus for the studied formulations.

## Conclusions

DGEBA epoxy resin formulations with anhydride-based hardeners were characterized targeting filament winding composite manufacturing. For all systems, the consumption of the oxirane ring band ( $915\text{ cm}^{-1}$ ) was observed during curing. The highest curing enthalpy was found for the E1H2 formulation, while the exothermic peak temperature was similar for all samples ( $143\text{ }^{\circ}\text{C}$ ). Thermal stability was improved with the H2 hardener. The E2H1 formulation exhibited higher loss modulus temperature ( $T_{\text{peak}}$  at  $88\text{ }^{\circ}\text{C}$ ) compared to other formulations ( $67 - 77\text{ }^{\circ}\text{C}$ ), and the tan delta  $T_g$  was higher for the E2 epoxy formulations ( $119\text{ }^{\circ}\text{C}$ ).

Additionally, viscosity at the processing temperature (60 °C) was slightly lower for the E1 resin. In DMA analysis, the E2H1 and E2H2 samples exhibited similar glass transition temperatures, but significant modulus differences were observed between the E2 resin formulations. The E1H1 sample showed the lowest tensile strength (~35 MPa), while the E2H1 and E2H2 samples showed slightly higher modulus (~3.5 GPa). Despite its higher viscosity at room temperature, the E2 resin performed similarly to other formulations at the processing temperature, demonstrating higher glass transition temperature, storage modulus, and thermal stability. In all, the E2H1 formulation was chosen as the best overall performance for the intended application.

### **Acknowledgment**

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