VISCOELASTIC BEHAVIOR OF LY5052 EPOXY RESIN IN RUBBERY STATE DURING CURING

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Abstract
The aim of the presented work is to investigate the relationship between the rubbery modulus and the degree of cure for partially to fully cured LY5052 epoxy resin. In particular, this work experimentally tests an existing model defined in shear modulus by redefining into the elastic tensile modulus. Experiments were performed in a Dynamic Mechanical and Thermal Analysis (DMTA) machine in the frequency domain. After the model is tested, super-master curves generated using time-temperature-cure superposition are normalized using the model so that the rubbery modulus made independent on the state of cure, which further simplifies the super-master curves. This results in a unique master curve that describes the viscoelastic behavior of the LY5052 epoxy resin for the given conditions. This consequently could help formulate simplified models to predict viscoelastic behaviour and also develop better experimental methodologies to characterize them.

1. Introduction

In modern composite manufacturing, the composite consists of two separate components, one being the matrix and the other being fiber. The matrix is usually a thermosetting resin polymer such as epoxy. In many commercial applications, the resin matrix is injected into a preheated mold that has been lined with a suitable reinforcing fiber either with the help of pressure or assisted by vacuum to produce the composite part. Other methods involve pre-impregnated sheets of fiber and matrix draped over a mold and cured. As the crosslink density of the resin increases and the liquid gels into a rubber-like state and finally into a solid glassy state when completely cured. It is generally understood that the residual stresses evolve more rapidly in the composite as the resin transitions from the rubbery state to the glassy state [1]. As cure progresses, the volume of the resin network decreases as result of the crosslinking pulling the long chain polymer networks together and restricting movement. This simultaneous increase in stiffness and the decrease in volume together contribute to increase in residual stresses especially if the material is subject to constraints imposed, for instance, by the molds or tools [2] or by the reinforcing fiber itself. Thus studying this transition region between the rubbery state and the glassy state in detail is important for the understanding of the evolution of residual stresses.

Evaluation of viscoelastic properties during cure has been modeled in multiple studies [3-9]. The cure state of a polymer has a direct influence on its physical properties. In the study of residual stresses and shape distortions in composite manufacturing, the region where the system transitions from the rubbery state into the glassy state is elsewhere most of the residual stresses build-up. As discussed earlier, the rubbery properties depend on the degree of cure above the point of gelation. As the degree

of crosslinking or cure increases by action of time and temperature on the polymer, the rubber modulus also increases since the enhanced chain networks will further resist any applied strain. In [3-4],[8] and [9], it was shown that the cure state can be used as a parameter while shifting in frequency or time to generate master curves, such that models can be developed based on time-temperature and degree of cure. When developing such a viscoelastic model to describe the evolution of material properties during cure, the variation of rubbery modulus will be problematic since one will be forced to consider including this variation into the model. As pointed out in [8], master curves can be shifted horizontally but additional shifting will have to be performed in the vertical direction to account for the dependence of the rubbery modulus with cure state. This in turn implies that more experimental characterization has to be performed.

The mechanics of the relationship between the rubbery modulus and degree of cure has been established by Adolf and Martin in [10-11], working with diglycidyl ether of bisphenol-A (DGEBA) and a diethanolamine hardener. Further, in their work in [12] they have employed these relationships to develop a constitutive model to calculate the evolution of residual stresses in crosslinking polymers. An experimental method to establish the relationship between degree of cure and the rubbery modulus has been developed by Sadeghinia et al. in [13]. In their work Sadeghinia et al. were able to experimentally verify the model developed by Adolf and Martin in [10] and [12] for a Novolac and bisphenol-A resin system. However, Mours and Winters [14] have argued that the models developed by Adolf and Martin were applicable only for systems with low molecular weight as high molecular weight systems did not tend to provide unique master curves. This argument was also confirmed experimentally by Mours and Winters in [15].

The work presented intends to analyze the relationship between the rubbery modulus and the degree of cure as derived by Adolf and Martin in [10] for the elastic tensile modulus. For this, the relationships developed by Adolf and Martin for the viscoelastic shear modulus will be redefined in terms of the viscoelastic tensile modulus, assuming Poisson's ratio to be constant in the rubbery region. Once the relationship is verified experimentally, the model will be used to normalize master curves developed through time-temperature-cure superposition (TTCS) [8] so that the variation in rubbery modulus due to varying cure states can be accounted for.

2. Method

2.1 Material

The resin system used in this study consisted of LY5052 epoxy with HY5052 hardener from Huntsman. According to the manufacturer, LY5052 is a blend of butanedioldiglycidyl ether and epoxy phenol novolac resin and HY5052 is a mixture of polyamines. Prior any experimental procedure, the resin was mixed in the ratio 100:38 by weight and stirred thoroughly, taking care not to include air bubbles.

2.2 DMTA testing

The thermo-viscoelastic characterization of the resin system was performed using a TA Instruments DMA Q800 instrument in single cantilever mode. A temperature scan using fully cured neat resin samples of LY5052/HY5052 was performed to obtain the relaxation curve. The scan was done at a frequency (f) of 1Hz and a temperature range of 23°C to 200°C in 10°C increments. Applied strain was of the order of 0.01%. After the background information for the fully cured material properties were determined, samples cured at two cure temperatures, 60°C and 80°C and various curing times as shown in Table 1were prepared. The test temperatures are selected in such a way that immeasurably little post-curing could occur while the DMTA test was being conducted. To further eliminate post-cure effects, fresh samples were used for each time scanning was performed at different test temperatures. Four testing temperatures were chosen viz. 23°C, 40°C, 60°C and 80°C at a frequency range of 200Hz, 100Hz, 10Hz, 1Hz and 0.1Hz with an applied strain of 0.01%. Following this,

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reduction in temperature and cure were performed to depict relaxation behavior at various cure state of the material.

Table 1: Curing times for testing

Temperatures	Curing times (hours)	Total number of samples
60°C	1.25; 1.5; 1.75; 2: 2.25; 2.5; 3	28
80°C	0.5; 0.75; 1; 1.25	16

In order to establish the viscoelastic models necessary to describe relaxation in various states of cure, subsequent data reduction was carried out by shifting the curves obtained in the frequency domain on the DMTA data. In TTC superposition, this reduction is performed twice, using two shift factors, one for temperature, a_T and one for cure, a_c. For most polymers, the temperature shift factor a_T is given by the Williams-Landel-Ferry (WLF) equation as given by

$$\log a_T(T) = \frac{-c_1(T-T_{ref})}{c_2+T-T_{ref}} \tag{1}$$

where T is the temperature and T_{ref} is the reference temperature. c_1 and c_2 are material constants dependent on the material under consideration. For the epoxy system LY5052/HY5052, these values are obtained as 77.59 and 433.6K respectively from experiments performed independently on fully cured resin samples. Just as one would expect the relaxation modulus to decrease with increasing temperature, it could be assumed that the effect of degree of cure on LY5052 was more or less similar to temperature with respect to the relaxation modulus. This is the basis for the second shifting or reduction in degree of cure with the aid of a cure shift factor. In [8] this cure shift factor was determined to be

$$\log a_c(T_c, t_c) = C * (t_c - t_{cref}), \tag{2}$$

where

$$C = 0.0026T_c^2 - 0.0903T_c + 1.39, \tag{3}$$

here T_c is the cure temperature, t_c is the time of cure and t_{cref} is the time of cure at which a reference cure state is attained. Considering the effects of both degree of cure and temperature on the relaxation modulus, the total shift a can be hence expressed as

$$\log a = \log a_T + \log a_c = \log(a_T.a_c). \tag{4}$$

3. Results and Analysis

The result from the temperature scan conducted on a fully cured epoxy sample is shown in Fig. 1. The plot shows the tensile storage moduli (E') with respect to temperature. The elastic storage modulus in the glassy region (E_g) at 23°C has been determined to be 2626.5MPa while the elastic storage modulus in the rubbery region (E_r) at 200°C has been determined as 19.952MPa.

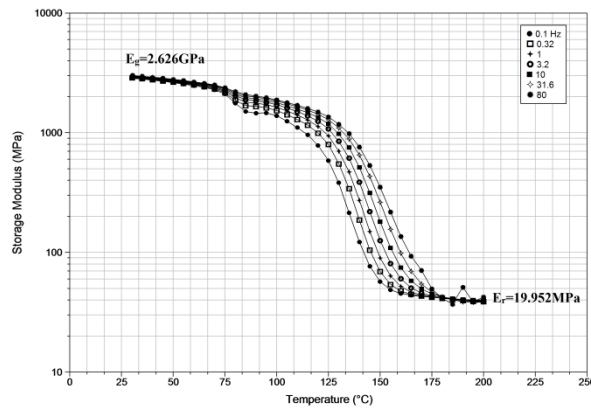Sibin Saseendran, Maciej Wysocki and Janis Varna

Figure 1. Elastic storage modulus vs. Temperature measured on a fully cured sample with the values of the glassy and rubbery modulus.

The scans performed on partially cured samples at various temperatures have also been analyzed. Fig. 2 shows an instance of samples cured at 60°C for 1.5hours (corresponding to a cure state of 85.74%) and scanned at various temperatures. These individual curves are then used to generate a master curve with 23°C as a reference shown in Fig. 3. The combined master curves for all the test cases for samples cured at 60°C and 80°C are put together, as shown in Figs. 4a and 4b.
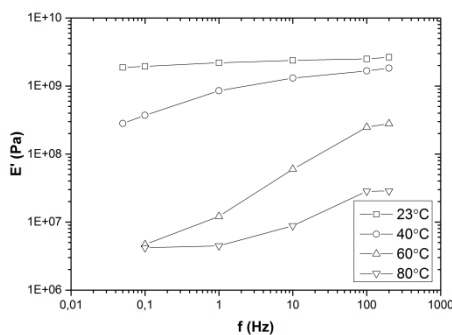

Figure 2. Frequency scans on samples cured at 60°C for 1.5hours (85.74%) with various testing temperatures.
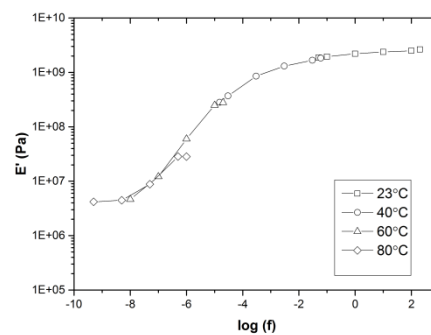
Figure 3. Master curve generated from the set shown in Fig. 2, with the curve at 23°C chosen as reference.

Shifting the curves in Figs. 4a and 4b again in cure time, results in a "super-master" curve. The reference state used for this second shifting is chosen as the time corresponding to an arbitrary 80% degree of cure at each temperature as shown in Figs. 5a and 5b. A more detailed description of the shifting procedure is explained in [8]. Here we note that the glassy plateau for all the curves overlap irrespective of the cure state of the material. However the rubbery plateau does tend to increase with increasing degree of cure (or cure times). The DMTA experiment was unable to fully capture the complete response in the rubbery state for all the cure states. However most of the experimental results progress sufficiently into the rubbery region while some tended to end somewhere in the transition region. The beginning of the rubber plateau of these curves was considered as the rubbery storage modulus.
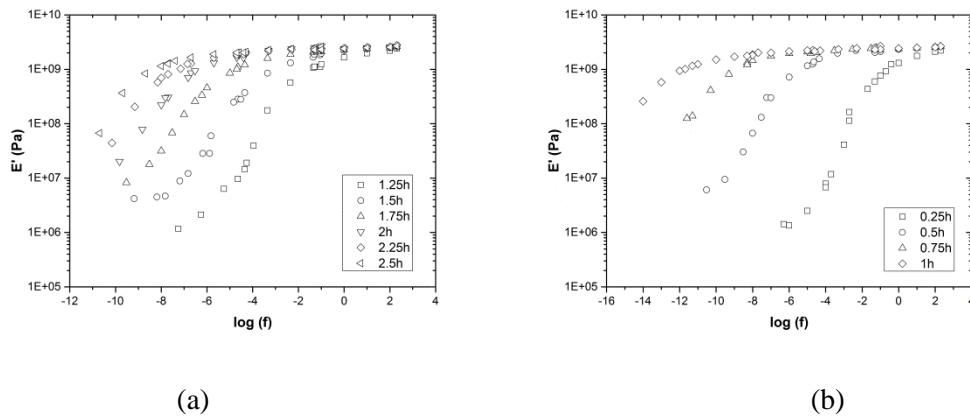
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(a)   (b)

Figure 4. Master curves for various cure states for samples cured at a) 60°C and b) 80°C, with 23°C testing temperature as reference state.

(a)   (b)
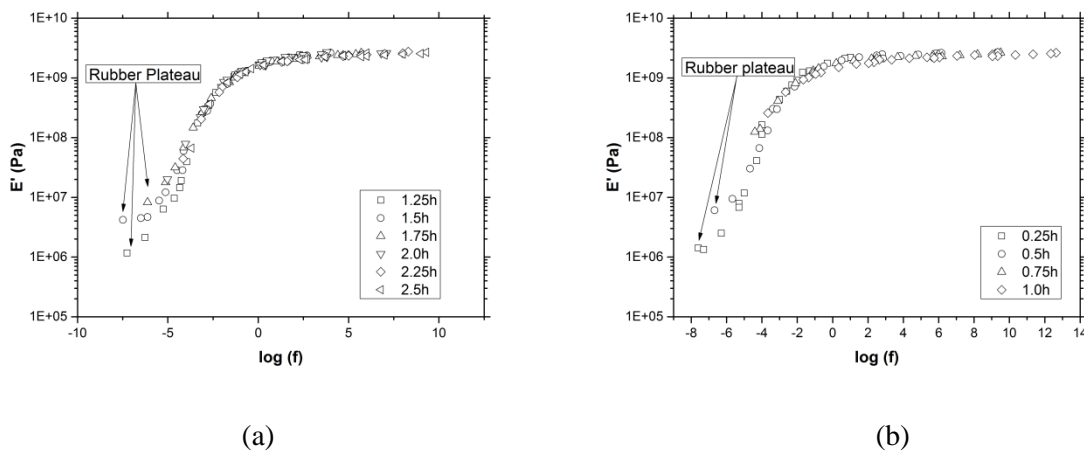
Figure 5. Super-master curves for experiments at a) 60°C and b) 80°C, referenced at 80% degree of cure, showing the start of the rubbery plateaus.

Table 2: Rubbery moduli determined from the beginning of the rubbery region from various cure states

Temperature	Cure time (hours)	Degree of cure	Rubber modulus (MPa)
60°C	1.25	0.8234	1.170
	1.5	0.8574	4.185
	1.75	0.8768	8.258
	2	0.8877	12.589
80°C	0.25	0.7070	1.338
	0.5	0.9051	6.065

The values of the rubbery storage modulus ($E'_r(\alpha)$) that were identified for both cure temperatures have been described in Table 2. The degree of cure corresponding to each cure time and temperature has been computed using the cure kinetic model by Kamal [8][18] which describes the reaction rate as an analytical function of temperature and degree of cure as shown in Eq. 5

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$$\frac{d\alpha}{dt}(T,\alpha) = Ae^{-\frac{B}{RT}}(\alpha^m)\left(\alpha_{T_g} - \alpha\right)^n, \tag{5}$$

where α is the degree of cure, A is the pre-exponential rate constant, T is the temperature in Kelvins, B is the reaction energy, R is the ideal gas constant, m and n are constants independent of cure temperature that are obtained from fitting experimental data from DSC experiments using standard least-squares fit. α_{T_g} is defined as the degree of cure attained for curing at various temperatures such that the material is in glassy state at the end of the curing cycle. The values of the constants and other parameters have been detailed in [8]. The values of $E'_r(\alpha)$ were then used against the model by Adolf and Martin [10] to determine if the values of the rubbery storage modulus for the given degree of cure obtained from experiment were in agreement. This scaling is given in terms of the shear modulus (G) in [10] as

$$G'_r(\alpha) = G^f_r\left(\frac{\alpha^2 - \alpha_g^2}{\alpha_{T_g}^2 - \alpha_g^2}\right)^{8/3}. \tag{6}$$

However, the tensile and shear moduli are related to each other linearly as $E = 2G(1 + \nu)$. Experimental evidence from previous work indicates that the viscoelastic Poisson's ratio in the rubbery region can be assumed approximately 0.5 for epoxy resins [17]. Thus Eq. 6 can be redefined in terms of the elastic modulus for the rubbery region dependent on the degree of cure $E'_r(\alpha)$ as given in Eq. 7. Furthermore Adolf and Martin have also stated in [10], [12] and [16] that the principles of time-cure superposition should be valid for all viscoelastic functions. Hence it can be deduced that

$$E'_r(\alpha) = E^f_r\left(\frac{\alpha^2 - \alpha_g^2}{\alpha_{T_g}^2 - \alpha_g^2}\right)^{8/3}, \tag{7}$$

where E^f_r is the rubbery modulus for a fully cured material and α_g is the cure state at which gelation occurs. From the DMTA test performed on a fully cured sample (see Fig. 1) E^f_r has been determined as 19.952MPa and α_g has been determined from independent rheometer experiments for LY5052/HY5052 epoxy system at 64%. Theoretically, the scaling is limited at the gel-point, below which the rubbery modulus is non-existent. The rubbery modulus obtained from experiment has been compared to the moduli obtained from Eq. 7 and the results have been plotted against each other in Fig. 6. It was noted that the model and the experimental results show fairly good agreement.

After the model was shown to be in sufficient agreement with experimental data, the next step is to further reduce the super-master curves shown in Fig. 5 into a normalized super-master curve. This was done by reducing the rubbery modulus and normalizing them using Eq. 8,

$$E'_n(t,T) = \frac{E(t,T,\alpha) - E'_r(\alpha)}{E_g - E'_r(\alpha)}, \tag{8}$$

where E_g is the elastic modulus in the glassy state of a fully cured resin and $E'_r(\alpha)$ is as computed and obtained using Eq. 7. The Eq. 8 was applied to each data point on the super-master curve to obtain the final normalized curve. The normalized curves for each cure temperature are shown in Fig. 6. We note here that all the curves overlap and reduce into a unique normalized super-master curve.
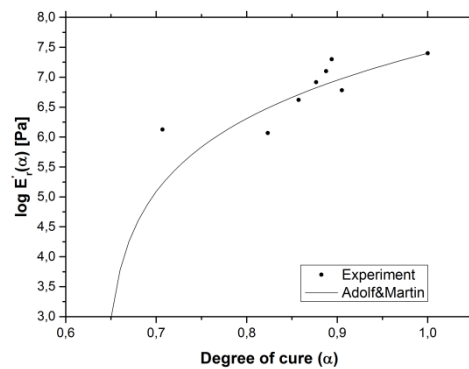
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Figure 6. Experimental values of the rubbery modulus vs. Adolf and Martin's model [10]
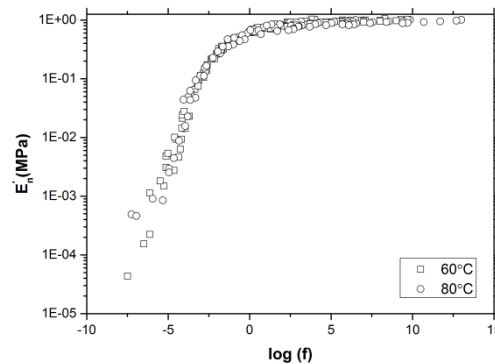

Figure 7. Normalized super-master curves with rubbery modulus reduction for the data sets at 60°C and 80°C

4. Conclusions

In this work the dependence of the rubbery elastic storage modulus on the degree of cure was investigated using data obtained from Dynamic Mechanical and Thermal Analysis (DMTA) experiments in single cantilever mode for various cure states. Super-master curves were generated using time-temperature-cure superposition in the frequency domain. The super-master curves indicate a dependency of the rubbery modulus on degree of cure. The model developed by Adolf and Martin [10] to show dependence of the rubbery plateau on the cure state was redefined from the shear modulus in terms of the elastic modulus, assuming Poisson's ratio remains constant ($\approx$0.5) in the rubbery region. After this, the model was used to compare with the experimental values of the rubbery modulus for various cure states. The experimental results are in good agreement with the model with slight discrepancies resulting from the fact that the actual rubbery limit determined from data may differ from the rubbery plateau modulus. Finally after establishing the dependence of the rubbery modulus on the degree of cure, the super-master curves were normalized and the rubbery modulus reduced to obtain true super master curves. The simplification of the super-master curve will be useful in characterizing material behaviour during cure for the LY5052 epoxy system and can be used to develop simple viscoelastic models. Such models can be really useful in delivering fast simulations for real world applications and make prediction of residual stresses and shape distortions during composite manufacture easier and accurate.

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