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Studies on the cure parameters of cyanate ester–epoxy blend system through rheological property measurements

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Abstract Thermosetting blend system of co-cured cyanate ester with epoxy resin is receiving importance for high technological applications because of its wide range of thermo-mechanical, rheological, and electrical properties. However, processing of these system warrant proper knowledge of the rheological behavior of the blend during the curing process. This article discusses the rheological behavior of the blend systems with respect to the pot life, gel time, gelation temperature and also evaluated fitting parameters for the prediction of gelation time and viscosity during the entire curing process from the isothermal rheological measurements.

Keywords Viscoelastic · Gel time · Engineering viscosity model · Castro–Macosko equation · Cyanate ester · Epoxy · Pot life

Introduction

The interpenetrating network of co-cured cyanate ester with epoxy resin possesses excellent dimensional stability, resistance to irradiation, low dielectric constant, low out gassing property endowed with wide range of physico-chemical, electrical, and thermal properties. Epoxy resins are one of the most widely used thermosetting polymers due to several factors like minimum pressure needed for fabrication of its products, low cure shrinkage, a wide range of curing temperature and curing agents which enables good control over the degree of cross linking and low cost. Because of these unique characteristics and excellent properties of these polymers, epoxy resins are used in structural adhesives, surface coatings, engineering composites, and electrical laminates. Improvement in thermal properties, moisture absorption, radiation resistance, and elastic modulus of epoxy resin has been investigated recently by modifying with a co-reactive component-cyanate esters. Cyanate esters possess good dielectric, thermal, and mechanical characteristics, low water absorption characteristics, excellent heat and radiation resistance, and low volume shrinkage; rendering them as a suitable material of choice in high-performance applications [1]. In addition to their excellent thermal stability, cyanate ester resins are relatively easy to process. Thus the co-cured cyanate ester–epoxy blend possesses excellent dimensional stability, resistance to irradiation, low dielectric constant, low out gassing property endowed with wide range of physico-chemical, electrical, and thermal properties. These characteristic properties make them amenable to produce advanced composites for applications in microelectronics, fusion relevant prototype magnetic winding packs as well as in space craft structures.

Pot life, gel time, gel temperature, viscoelastic properties, curing temperature, and curing time are some of the important parameters for the processing of thermoset resins. Pot life is defined as the period of time that a formulated material can be processed safely. Gelation occurs at a particular point during cure when an infinite and insoluble molecular network is formed [2, 3]. Upon gelation, macroscopic flow becomes impossible and stress relaxation becomes difficult. So the accurate determination of the gel point becomes very

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important as the polymer can be easily shaped or processed only before the gel point, where it can still flow and can be easily deformed with stresses applied. It also allows the estimation of the optimal temperature and time for which the sample should be heated before being allowed to set in the mold. Thus, both from scientific and technological viewpoints, it is necessary to determine the gel point accurately and to understand the behavior of the resin upon gelation.

Various methods are reported for measuring the gelation time like differential scanning calorimetry, infra red spectroscopy, rheology, and visual observation using oven curing and rheological methods. The most sensitive and reliable method is dynamic rheological testing. Using this method, the gelation process can be monitored by the changes in rheological properties as a function of temperature or time. Only a few number of works has been reported on the rheological properties during curing of cyanate ester blend system.

Thus, systematic study on the cure parameters of CE–epoxy system by the rheological property measurement is receiving importance. Various rheological methods have been used to determine the gel point and they usually are based on definitions and approaches, including the determination of the divergence point of the steady-state shear viscosity or normal stress, the crossover point of the dynamic storage modulus and loss modulus, the point at which the loss tangent becomes independent of testing frequency, or the crossing point between the base line and the tangent drawn from the turning point of storage modulus curve [4, 5].

A range of rheological models had been presented for predicting the viscosity of thermosetting resin during the liquid molding process, including empirical models, probability-based model, gelation models, and models based on free volume analysis. For isothermal cure, the predominant models are the empirical models. The commonly used empirical models for the epoxy resin are the dual-Arrhenius rheological model and the engineering viscosity model as they can be established to predict the viscosity without the need for determining the resin cure kinetics [6, 7]. The equations of those are simple and the model parameters can be obtained from isothermal viscosity–time measurements. However, these models could predict viscosity increase only in the initial stage of the curing process and failed to predict it in the later stage. Castro and Macosko have suggested a chemorheological model to predict the viscosity variation for the entire curing process. Castro and Macosko [8] studied the cure-kinetic process of liquid dicyanate resin by developing an empirical relation. They developed this equation by employing the kinetic and rheological data during curing for predicting the viscosity variation during the entire curing process.

In this article, we report the pot life, gel time, gelation temperature, viscoelastic properties, curing temperature, and curing time of the 60:40 (epoxy:cyanate ester) blend system during the curing process by rheological measurement under isothermal conditions. Fitting parameters for predicting the gelation time for particular temperature were evaluated. Further, an engineering viscosity model and Castro–Macosko-type equation model was used to obtain the fitting parameters for prediction of the variation of viscosity during the isothermal curing process.

Experimental methods

Materials

Arocy L-10 and Araldite PY-306 were supplied by Huntsmans Advanced Materials, America Inc, 8600 Gosling Road, Texas. The catalyst used for curing is manganese acetyl acetonate along with nonylphenol as co-catalyst, supplied by Alpha UK Hemarsh Technologies.

Sample preparation

Mn-acetylacetonate was dissolved in nonylphenol at a molar ratio of 25:1 (nonylphenol:Mn-acetylacetonate) at 80 °C for 1 h. Cyanate ester (Arco L-10) and bisphenol-F epoxy (PY306) were mixed in 60:40 (Epoxy: cyanate ester) mass proportions and 0.1 mass% catalyst with respect to the mass of blend was added dropwise and was heated at 60 °C for 30 min. Metal concentration ranging from 20 to 300 ppm based on resin content was fixed.

Rheometry

Apparent viscosity, complex viscosity, storage modulus, and loss modulus of the CE–epoxy blend systems during non-isothermal and isothermal curing were monitored rheometrically using Anton Paar Physica MCR 150 rheometer with disposable parallel stainless steel plates of 50 mm diameter, and the gap height between parallel plates was set at 1 mm. Rheological measurements were done in dynamic oscillatory mode under time sweep (isothermal). Experiments were performed with strain amplitude of 1 % and an angular frequency of 10 s^{-1}. Pot life was studied by measuring apparent viscosity under isothermal conditions (70 °C) in rotatory mode at a constant shear rate 200 s^{-1}.

Results and discussion

Rheological properties during the curing process of CE–epoxy blend system were studied using rheometer under non-isothermal and isothermal conditions. The cure reaction mechanism between the CE and epoxy resin is very complex. In our earlier reports, we have shown that the main reactions occurring during CE–epoxy curing are (1) trimerization of cyanate into triazine, (2) insertion of glycidyl ether of epoxy into cyanurate, (3) isomerisation of alkyl substituted cyanurates to isocyanurates, (4) build up of oxazolidinone, (5) phenol abstraction, (6) phenol glycidyl ether addition. The schematic representation of the mechanism is shown in Fig. 1. Formation of the various products during curing was studied by performing FTIR spectroscopy which revealed that the finally cured product consists of a mixture of oxazoline, oxazolidinone, and triazine in varying proportions according to the composition of CE–epoxy in the blend system [9, 10]. Proper knowledge about the rheological properties is receiving importance for understanding and hence tuning the curing process for deciding the properties of the end products. The various parameters measured by rheology during the curing process are described below.

Pot life

The change in viscosity as a function of time at a given temperature can be used to predict the period of time during which the resin may be safely used (pot life). Apparent viscosity measurements were performed for various compositions under rotational mode at 70 °C and the profile showing viscosity versus time curve is shown in Fig. 2. Viscosity is observed to be independent of time for 1 h at 70 °C instructing that viscosity of the blend system is secure for more than an hour revealing sufficient processing time for the system. All the compositions showed same trend in the viscosity variation with time. The viscosity value observed to be in the decreasing order of 60:40 (0.0310 Pa s) > 90:10 (0.024 Pa s) > 50:50 (0.0215 Pa s) > 80:20 (0.0207 Pa s) (epoxy:cyanate ester)

Evaluation of fitting parameters for the prediction of gel time

As mentioned in the introduction section, there are various methods to establish the gel point of a system. In this experiment we have used the point of intersection of the base line and the tangent at the point of deflection of the storage modulus curve as the gel time. Rheological properties during curing of epoxy:cyanate ester system (60:40) are studied under both non-isothermal and isothermal conditions. Rheogram showing the variation of storage modulus, loss modulus, and complex viscosity with respect to temperature is shown in Fig. 3. It was observed that during curing of the blend, the storage modulus increased insignificantly at the beginning and later on rises to a maximum value. This increase in storage modulus is attributed due to polymerization which will lead to gelation. A fluctuation in storage modulus is observed immediately after this maximum and again it showed an improvement in its values. This depression is believed to be due to the partial phase separation of the formed high molecular mass polymer from the matrix during the curing process. It can be observed that there is no change in the values of rheological properties at lower temperature.

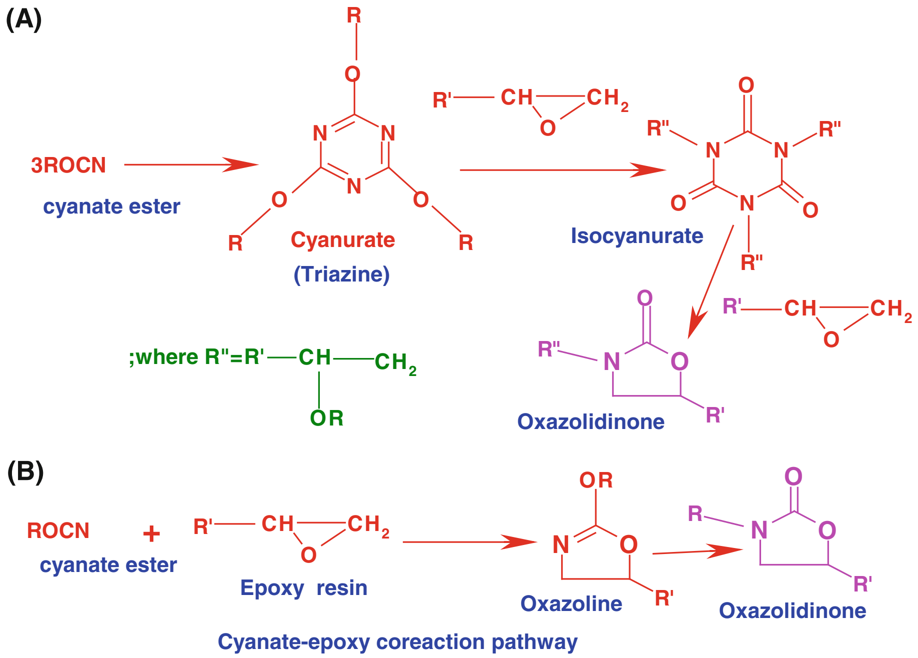

Fig. 1 Epoxy–cyanate ester reaction pathway

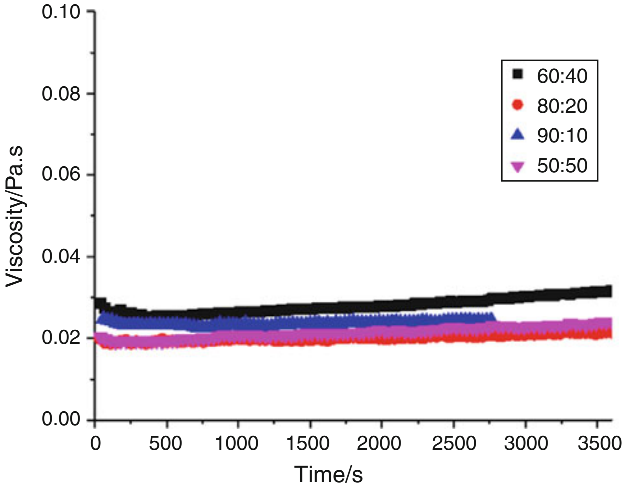

Fig. 2 Plot of variation of viscosity with time for the determination of storage time of various epoxy:cyanate ester blend compositions

Rheogram exhibited quick change in rheological properties when temperature reached to 198 °C, which is attributed due to gelation. Thus, the rheological behavior during the curing process can be classified into three regions: (1) initial stage to the point where storage modulus of the mixture gradually increased and then it reaches a local maximum, (2) after that, these moduli slightly decreased which can be attributed due to vitrification, and (3) finally storage modulus again increased because of the extensive network formation during the final curing of the CE–epoxy blend. Thus the viscoelastic behavior of the blend system could clearly define the change in the curing process. The value of the rheological properties during non-isothermal curing of the blend is given in Table 1.

In order to determine the main rheological changes during the isothermal curing of CE–epoxy blend systems, time sweep experiments at various isothermal curing temperatures of 150–190 °C were performed. The variation of storage modulus with time at various isothermal curing temperatures was obtained from these experiments. Gel time of the blends at various temperatures was obtained from the crossing point between the base line and the tangent drawn from the turning point of storage modulus curve and is given in Table 2. It shows that as the curing temperatures increased, the time taken for gelation decreased. Gel time test revealed that blend cured in presence of catalyst exhibited less time for samples cured in the absence of the catalyst.

The activation energy for the crosslinking reaction can be calculated from the measurement of the gel time at different temperatures using the method suggested by the researchers [11, 12]. However, this conclusion is based on the assumption that the curing kinetics involves only a single reaction. But the activation energy calculated can be considered as a representative of the multiple reactions in progress. Thus relationship between t_{ge1} [13] and temperature agrees with Arrhenius law given by Eq. (1)

$$t_{\mathrm{gel}} = k \exp\left(\frac{E_{\mathrm{a}}}{RT}\right), \tag{1}$$

where k is the pre-exponential factor, E_{a} is the apparent activation energy, and R is an ideal gas constant. The following equation could be obtained by taking the logarithm on both sides of Eq. (1):

$$\ln t_{\mathrm{gel}} = \ln k + \left(\frac{E_{\mathrm{a}}}{RT}\right) \tag{2}$$

The activation energy E of curing can be calculated from the slope of the plot of logarithm of gel time against ($1/T$), as shown in Fig. 4 [16]. The values thus obtained are

Fig. 3 Variation of storage modulus, loss modulus, and complex viscosity with temperature for the non-isothermal curing of the 60:40 (epoxy:cyanate ester) blend system in the presence of catalyst

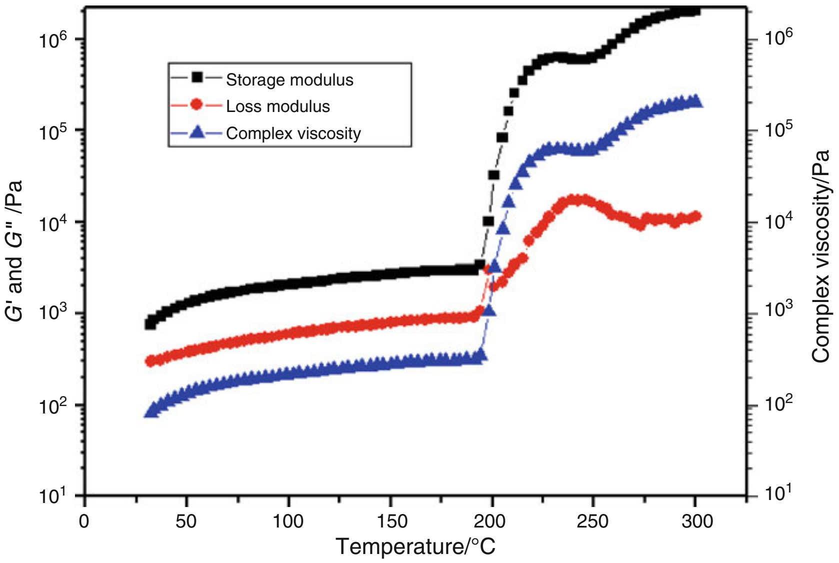

Table 1 Values of rheological parameters during non-isothermal curing of 60:40 (epoxy:cyanate ester) blend system in the presence of catalyst

	Temperature/°C	Storage modulus/Pa	Loss modulus/Pa	Complex viscosity/Pa
Gelation	239	6.31×10^5	1.71×10^4	6.31×10^4
Final curing	283	1.77×10^6	1.03×10^4	1.06×10^4

Table 2 Gel time of 60:40 blend systems at various curing temperatures

Curing temperature/°C	Gel time/s	
	Without catalyst	With catalyst
150	3,920	2,638
160	3,524	2,457
170	3,319	1,944
180	3,108	1,151
190	1,518	941

shown in Table 3. The activation energy of system employing catalyst was found to be less than systems without catalyst.

Thus the gel time–temperature relationship could be mathematically expressed as: For systems with catalyst:

$$t_{\mathrm{gel}} = 6.78 \times 10^{-3} \exp\left(\frac{50713}{R} \times \frac{1}{T}\right) \tag{3}$$

For systems without catalyst:

$$t_{\mathrm{gel}} = 2.67 \times 10^{-3} \exp\left(\frac{45731.4}{R} \times \frac{1}{T}\right) \tag{4}$$

Accordingly, the gel time at any isothermal curing temperature could be predicted directly from Eqs. (3) and (4).

Table 3 Apparent activation energy of 60:40 blend systems

60:40 Blend system	Activation energy, E_a/J mol^{-1}
Without catalyst	50,713
With catalyst	45,731.4

Prediction of viscosity during the isothermal curing process

Here viscosity variation during the isothermal curing process was determined under isothermal condition using oscillatory method under 1 % amplitude strain and a constant angular frequency of 10 s^{-1}. Here, we have used two model equations for evaluating fitting parameter from experimental results: (1) engineering viscosity model, (2) chemorheology model.

Variation of complex viscosity during the curing of the 60:40 CE–epoxy blend system at different isothermal temperature in the presence of catalyst was also found. It was observed that the complex viscosity of the blend system progressively increased with time and exhibited a sudden increase in viscosity after gelation.

Engineering viscosity model

Attempts were done to predict the viscosity of blend during curing process using an engineering viscosity model

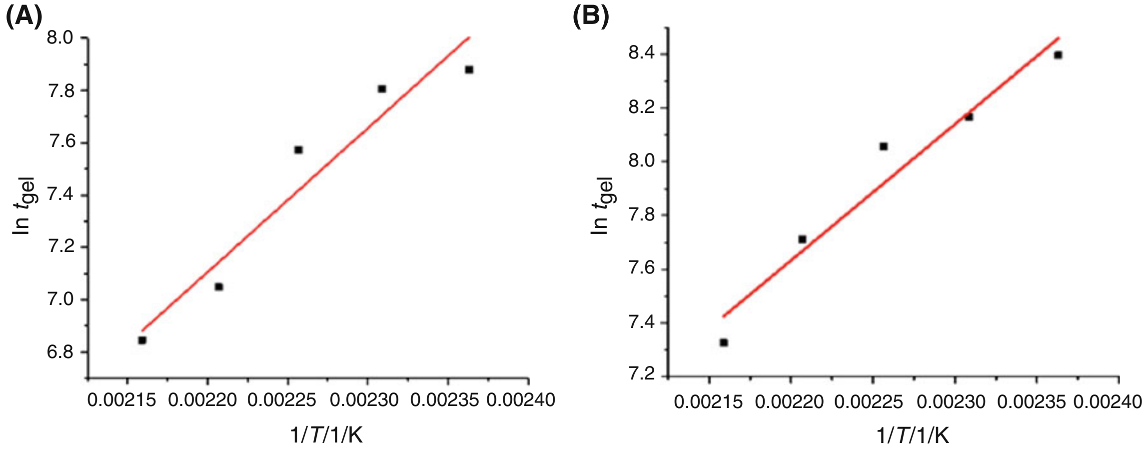

Fig. 4 Plot of logarithm of gel time versus reciprocal of curing temperature for 60:40 (epoxy:cyanate ester) systems: **a** with catalyst, **b** without catalyst for the calculation of activation energy

equation [13–15]. It was assumed that the viscosity was made up of two parts, the original viscosity (the viscosity at zero time) and the increment of the viscosity caused by the chemical reaction. The equation of the engineering viscosity model is shown below:

$$\eta(T,t) = \eta(T) + C \cdot \exp\left[B(T)t\right] \tag{5}$$

where C is the coefficient of the change of the viscosity, $B(T)$ is the chemical reaction variable which is related to temperature. At isothermal conditions Eq. (5) can be expressed as:

$$\eta(t) = \eta_0 + C \cdot \exp\left(B \cdot t\right) \tag{6}$$

where $\eta(t)$ is the viscosity at any time t and η_0 is the initial viscosity or the original viscosity.

The effect of curing temperature on the viscosity of the resins can be fitted to an Arrhenius temperature-dependent viscosity function based on the temperature dependence of the initial viscosity [8], and the initial viscosity η_0 is expressed as

$$\eta_0 = k_1 \exp\left(\frac{k_2}{T}\right) \tag{7}$$

The logarithm of the above equation is taken:

$$\mathrm{Ln}\ \eta_0 = \ln k_1 + \frac{k_2}{T} \tag{8}$$

Graph is plotted using ln η_0 versus $1/T$ as shown in Fig. 5, k_1 and k_2 are obtained from the intercept and slope of the linear plot (Fig. 5).

Thus the relationship between initial viscosity of the resin and the curing temperature can be presented as:

$$\eta_0 = 6.13 \times 10^{-9} \exp\left(\frac{8343.73}{T}\right) \tag{9}$$

Nonlinear curve fitting of the complex viscosity versus time plots based on Eq. (6) was applied to determine the parameters B and C of the engineering model for every curing temperature. The fitting parameters thus obtained are tabulated in Table 4.

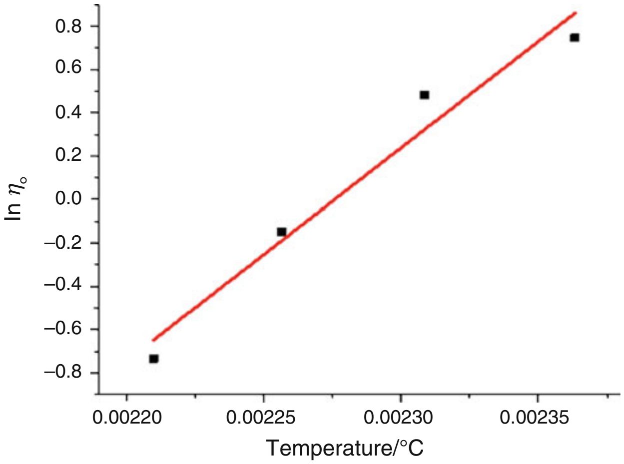

Fig. 5 Relationship between logarithm of initial viscosity versus reciprocal of curing temperature of epoxy–cyanate ester blend system

The parameters B and C can be expressed mathematically by the below functions

$$B = k_3 \exp\left(\frac{k_4}{T}\right) \tag{10}$$

$$C = k_5 + k_6 T \tag{11}$$

The mathematical parameters k_3 and k_4 were calculated from the linear fitting plot of ln (B) versus $1/T$ and k_5 and k_6 from the linear fitting of C versus T plot.

All these parameters were taken into Eq. (6), and the final equation for the engineering viscosity model can be presented as follows:

$$\begin{aligned}\eta(t) = {} & 6.13 \times 10^{-9} \exp\left(8343.73/T\right) \\ & + \left[(-13571) + 31.85\,T\right] \\ & \cdot \mathrm{Exp}\left[1.13 \times 10^{-5} \exp\left(1235.6/T\right) t\right]\end{aligned} \tag{12}$$

In Fig. 6, the experimental data of viscosity–time of the blend system at five different temperatures are compared with the predicted theoretical values derived from the engineering viscosity model. It was observed that the data calculated from the engineering model matched with the experimental data at the initial stages of the curing process and later, it deviated from the model.

Chemorheology model (Castro and Macosko equation)

To predict the variation of viscosity for the entire curing range, a chemorheological model was developed by Castro and Macosko [8]. This model combines the kinetic and rheological effects during the curing process.

Actually the viscosity variation during the curing process depends on both the curing process and the state of polymerization. So we assume that the viscosity is a function of temperature and conversion.

$$\eta = \eta(T, \alpha) \tag{13}$$

Temperature influences viscosity in two opposing ways. Rising the temperature will cause viscosity to drop at a given conversion but will increase the reaction rate, causing an increase in conversion and viscosity. To

Table 4 Parameters of engineering viscosity model

Temperature/°C	*B*	*C*
150	0.000685	3.94
160	0.00063	60.38
170	0.000612	583
180	0.000508	891.47
190	0.000488	1,180

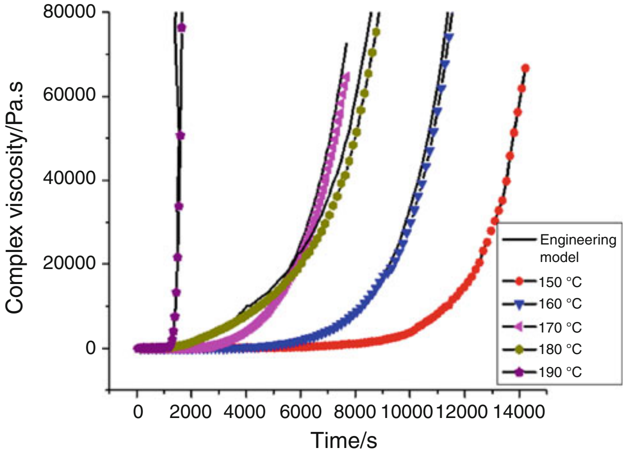

Fig. 6 Comparison of engineering viscosity model and experimental data prediction of complex viscosity versus time plots of the blend system

Table 5 Parameters of chemorheological model

60:40 Blend	A_0/Pa s	E_0/J mol^{-1}	A	B	α_g
With catalyst	6.13×10^{-9}	69,369.8	9.55	1.2	0.62

separate these effects, it is proposed that the viscosity should be explicitly related to reactive group conversion. For this, the variation of viscosity and extent of conversion must be monitored at the same temperature based on the following empirical relation:

$$\eta = A_0 \exp\left(\frac{E_0}{RT}\right)\left[\left(\frac{\alpha_g}{\alpha_g - \alpha}\right)^{A+B\alpha}\right] \tag{14}$$

where α is the conversion, α_g is the conversion at gel point, A_0 and E_0 are the frequency factor and activation energy, respectively, where A and B are constants. The first term or the temperature dependence of viscosity in the above equation corresponds to the Arrhenius temperature–viscosity relation shown in Eq. (7). Thus we can equate initial viscosity as:

$$\eta_0 = A_0 \exp\left(\frac{E_0}{RT}\right) \tag{15}$$

The A_0 and E_0 values are obtained from the initial viscosity plot (Fig. 5). Consequently we can rewrite Eq. (16) as:

$$\frac{\eta}{\eta_0} = \left(\frac{\alpha_g}{\alpha_g - \alpha}\right)^{A+B\alpha} \tag{16}$$

where $\frac{\eta}{\eta_0}$ is the ratio of the complex viscosity of the blend during the curing process. To obtain the conversion dependence of viscosity, the variation of viscosity and extent of reaction were monitored at the same temperature.

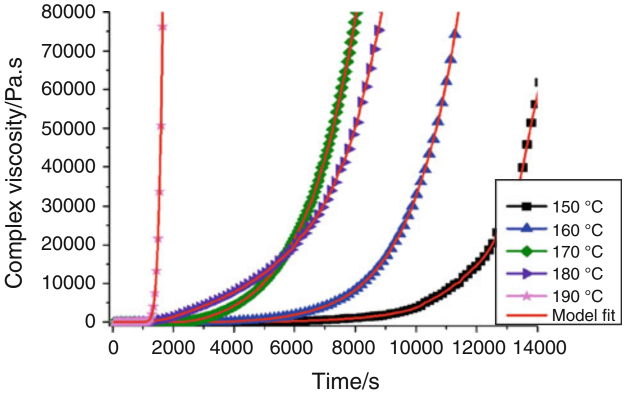

Fig. 7 Comparison of experimental data and chemorheological model prediction of complex viscosity versus time plots of the blend system

The extent of reaction was obtained at the same temperature from the isothermal dynamic scanning calorimetric analysis [9, 10]. The conversion values obtained from DSC plots are plotted against $\frac{\eta}{\eta_0}$, to evaluate the constants A, B, and α_g by curve fitting procedure. The parameters thus obtained are tabulated in (Table 5). These fitting parameters were established by plotting the predicted viscosity values and experimental values against time as shown in Fig. 7. It was found that the predicted values were exactly matching with the experimental values during the entire curing process.

Conclusions

Studies on the variation in the rheological properties during the progress of curing process of thermoset blend is receiving importance, since it helps in controlling the process parameters which will decide the end properties of the products. Pot life for 1 h at 70 °C is established by observation of viscosity independent time plot at constant temperature. Gelation time of the blend system evaluated from the tangent of G' versus time curve revealed that increase in the isothermal curing temperature showed a plunge in the gelation time. Fitting parameters were evaluated for predicting the gelation time for every isothermal curing temperature. The apparent activation energy during gelation was found to be less for system conducted in the presence of catalyst. During the curing process, the storage modulus of the system increased at a higher rate than the loss modulus, justifying that as the blend solidifies, the elastic nature increased. Fitting parameters for the prediction of viscosity during the progress of curing process were evaluated using engineering model and Castro–Macosko-type equation model. Results revealed that engineering viscosity model was simple in form but could not determine the variation of viscosity accurately after a particular conversion. However, the Castro–Macosko-type equation model could describe the isothermal viscosity rise for the entire curing process and can be used determine the viscosity during the mold filling stage of any thermosetting systems.

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