

Study of the Curing Kinetics of Epoxy Resins with Biobased Hardener and Epoxidized Soybean Oil

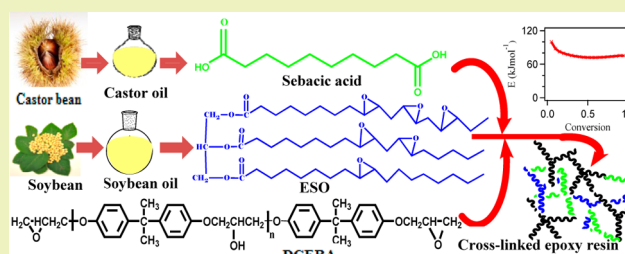
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ABSTRACT: The goal of this research was to study the kinetics of the reaction of diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin cured with sebacic acid as a biobased hardener in the presence of three different loadings of epoxidized soybean oil (ESO) (i.e., 10, 20, 30 wt %). Nonisothermal differential scanning calorimetric (DSC) and model-free isoconversional method was used to analyze the curing kinetic data and determine the activation energy of the reactions. It was found that the biobased hardener increased the enthalpy of reaction as well as the activation energy of reaction in comparison to the amine hardeners that are currently used for epoxy curing. The addition of epoxidized soybean oil increased the enthalpy of reaction, maximum exothermic temperature, and activation energy of the system. Kissinger–Akahira–Sunose (KAS) and Starink methods were used to determine the activation energy of the studied systems. It was also found that the curing reaction of epoxy with 30 wt % of ESO is diffusion controlled in comparison with other counterparts.

KEYWORDS: Epoxy resin, Epoxidized soybean oil, Differential scanning calorimetry, Reaction kinetics, Activation energy, Thermoset polymers, Biobased materials



INTRODUCTION

In recent years, the significant emphasis on environmental issues, limitation of nonrenewable resources, greenhouse gas emissions, climate change, and concern about waste disposal has led to substituting petroleum-based materials with their biobased counterparts on the basis of cost performance.^{1–5} Among the different petroleum-based resins, epoxy resins are thermoset polymers that are well known due to their superior properties such as high adhesive strength, tensile strength, stiffness, electrical strength, and acceptable heat and chemical resistance. Epoxy resins have versatile industrial applications such as adhesives, electronics, coatings, and composites. One of the main drawbacks of epoxy resin is its brittleness. The addition of some functional vegetable oils such as epoxidized soybean oil can improve the toughness of epoxy resin while increasing the biobased content of the final composites.^{2,6} Epoxidized soybean oil is the product of the conversion of the double bonds of soybean oil, a triglyceride of saturated and unsaturated fatty acids into oxiran groups. ESO has been manufactured for more than 30 years and is commercially available under different trade names.⁷ The substitution of this biobased thermoset resin with petroleum-based epoxy resin can also decrease the production costs of the final engineering composites due to the lower cost of soybean oil and its abundance.

In addition, most of the common curing agents of epoxy resins such as aliphatic and aromatic amines and anhydrides are fossil fuel based and toxic. Exposure to these materials can have

negative effects on human health such as rhinitis, conjunctivitis, and asthma.⁸ Considering the importance of using biobased materials in industrial applications and attempts to move toward sustainability, it will be important to find a biobased hardener to substitute for the nonrenewable-based hardeners. Jaillet et al.⁹ reported the synthesis of biobased carboxylic acid from vegetable oils as a hardener of epoxy resin and its application in the coating industry. Li et al.⁸ synthesized a lead-free amino acid as the curing agent of epoxy resin in an electronic application. Continuing this research path, we are introducing sebacic acid as a hardener of epoxy resin. It can be manufactured from the heating of castor oil up to 250 °C with alkali and has been used to produce nylon 6–10.^{10–12} This biobased acid has a wide range of applications in the manufacturing of biodegradable polyesters,¹³ elastomers,¹⁴ lubricants, and compatibilizers.^{10,15} In addition, the cost of sebacic acid is comparatively lower than some common amine hardeners. Therefore, sebacic acid can be a good choice because it is biobased and able to react with epoxy resin. The carboxylic groups of this biobased curing agent can react with oxiran groups of epoxy resins with a nucleophilic mechanism and form a cross-linked network.^{9,16}

The study of the kinetics of curing of a thermoset resin has significant importance in developing and optimizing curing

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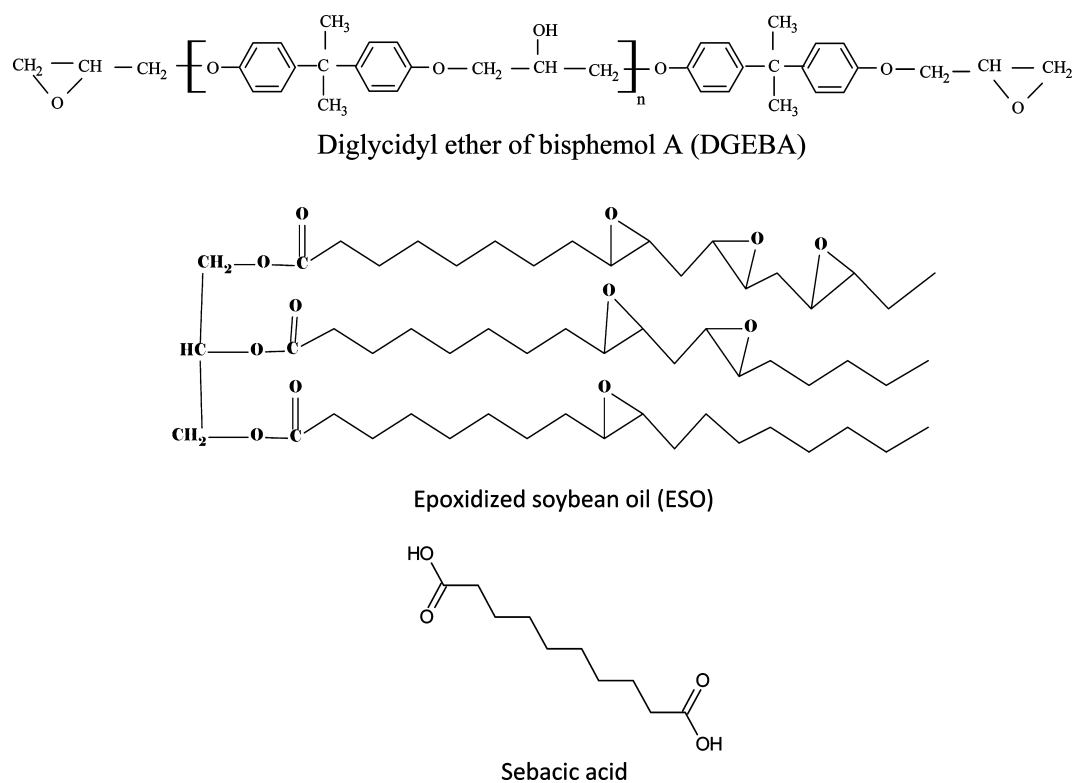


Figure 1. Schematic chemical structures of the raw materials.

cycles in the industrial manufacturing process.¹⁷ It can help to improve the quality of the final product as well as process development.¹⁸ The curing kinetic models can be used to minimize the curing cycle and be used with heat transfer and chemorheological models to reduce the internal stress in composites during the manufacturing process and lead to improved properties and performances of the final products.^{17,19–24} There are various methods to investigate the curing kinetics of thermoset resins such as dielectric analysis (DEA), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), and ultrasonic methods.²⁵ DSC is among the most common methods in the determination of kinetic parameters.

Although there are various studies on the curing of epoxy resins with different hardeners, to the best of our knowledge there is not any kinetic study on the curing of a mixture of epoxy resin and ESO with a biobased hardener. Clear understanding of the curing behavior of this system can be helpful in composite development and industrial manufacturing processes as well as quality control optimization. In this paper, the curing kinetics of epoxy resins and sebacic acid as a biobased hardener in the presence of different amounts of ESO were studied by DSC, and the dependence of the curing activation energy with conversion with different approaches was identified.

EXPERIMENTAL SECTION

Materials. Epon 828, the diglycidyl ether of bisphenol A (DGEBA), was purchased from Hexion Specialty Chemicals and used as a main component. An amount of 10–30 wt % of DGEBA was substituted for epoxidized soybean oil (ESO, Vikoflex 7170), which was kindly supplied by Arkema. Sebacic acid was purchased from Fisher scientific and used as received. 1-Methyl imidazole was purchased from Sigma-Aldrich and used as an accelerator. The amount of curing agent was calculated theoretically based on the

stoichiometry. The chemical structures of raw materials are presented in Figure 1.

Characterization. The curing behavior of epoxy/ESO/sebacic acid was investigated by differential scanning calorimeter (DSC Q-200, TA Instruments, Inc.). The experiments were performed under nitrogen atmosphere with a flow rate of 50 mL/min; the sample weight was between 3 and 5 mg. In dynamic experiments, the samples were heated from 25 to 275 °C at various heating rates (i.e., 2.5, 5, 7.5, and 10 °C/min). The total area under exothermic peak of the DSC graph was considered as the total heat of the reaction. Conversion in a specific time was calculated by the determination of the area under the exothermic peak at that data point by the “integrate peak” option in TA Universal Analysis software and dividing it by the total heat of reaction. The isothermal experiments were performed at different temperatures (i.e., 150, 165, and 185 °C). In these sets of experiments, the thermal program was started by increasing the temperature from 25 °C to the preferred temperature with the heating rate of 60 °C/min, following with the isothermal condition. When the curing reaction was completed, the samples were cooled to 20 °C with a cooling rate of 10 °C/min. In the next step, the dynamic experiment was performed with the heating rate of 10 °C/min in order to determine the residual heat of reaction and glass transition temperature of the cured samples.

Theory of Kinetic Analysis. Kinetics of a reaction presents the relationship between process rates and different parameters. Generally, the rate of reaction can be formulated by three different variables, i.e., temperature, T ; extent of conversion, α ; and pressure, P , as shown in eq 1.²⁶

$$\frac{d\alpha}{dt} = k(T)f(\alpha)h(P) \quad (1)$$

It should be mentioned that the majority of the kinetics methods ignore pressure dependence, so the rate of reaction can be presented by only two variables, i.e., T and α .

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

The function of $k(T)$ can be easily described by the Arrhenius equation.²⁷

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (3)$$

where R is the universal gas constant, and A and E are the pre-exponential factor and activation energy, respectively. The function of $f(\alpha)$ can be exhibited by various reaction models.²⁸ The main drawback of these model fitting techniques is the “kinetic compensation effect” that can be seen especially under dynamic conditions.¹⁷ It is also worth pointing out that the application of model fitting methods can be challenging when the reaction is multi-step. In this case, the computational methods that can detect multi-step processes should be used.²⁹ According to the ICTAC kinetic project,³⁰ isoconversional methods also called model-free kinetics methods (MFK) are one of the best methods to overcome the discussed challenges. The isoconversional methods are used to study the change of activation energy with temperature and conversion during the curing reaction. Model-free methods also allow for identifying whether the curing is reaction controlled or diffusion controlled.¹⁷ The most common methods in this approach are Friedman, Ozawa, and Flynn and Wall.²⁹ All model-free methods are based on the fact that the reaction rate is only a function of temperature at a constant extent curing degree.³¹ Taking the logarithmic derivative of the reaction rate (eq 2) at a constant conversion extent easily gives eq 4, where α represents the values at a given conversion.

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}}\right]_{\alpha} = \left[\frac{\partial \ln k(T)}{\partial T^{-1}}\right]_{\alpha} + \left[\frac{\partial \ln f(\alpha)}{\partial T^{-1}}\right]_{\alpha} \quad (4)$$

Considering the principle of the isoconversional method, it can be easily found that $f(\alpha)$ is constant at a constant conversion extent. Thus

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}}\right]_{\alpha} = -\frac{E_{\alpha}}{R} \quad (5)$$

Because there is no analytical solution in the isoconversional approach, the different authors proposed the various equations based on approximation of the temperature integral.^{32,33} According to the ICTAC kinetic project,²⁶ it is recommended to use the Kissinger–Akahira–Sunose (KAS) (eq 6) and Starink (eq 7) methods due to higher accuracy.

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \text{Const} - \frac{E_{\alpha}}{RT_{\alpha}} \quad (6)$$

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^{1.92}}\right) = \text{Const} - 1.0008\left(\frac{E_{\alpha}}{RT_{\alpha}}\right) \quad (7)$$

where β is the heating rate.

RESULTS AND DISCUSSION

In this study, the kinetic parameters of epoxy samples containing biobased hardener and different loadings of epoxidized soybean oil were investigated. All plots of conversion vs time for various heating rates exhibited the autocatalytic model. An example is shown in Figure 2. The curing characterizations of samples are shown in Table 1. According to this table, it is easily shown that the total heat of reactions are almost the same at various heating rates. As shown, the onset of reaction (T_{onset}), reaction termination temperature (T_{end}), and exothermic peak temperature (T_{p}) increased as the heating rate increased. This increase is widely described in the literature^{17,34} and can be attributed to the delay in the instrument response at a higher heating rate. It also can be found that the addition of ESO decreased the enthalpy of reaction. This can be due to higher epoxy equivalent weight of

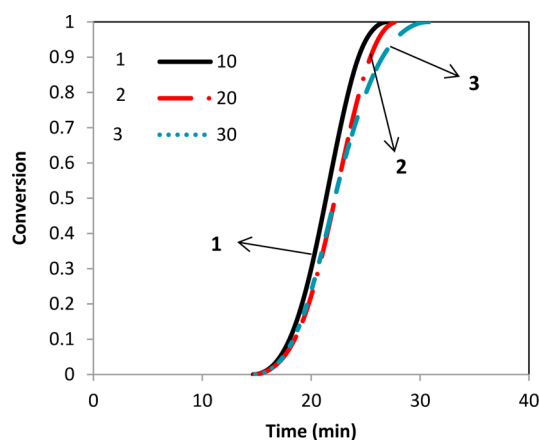


Figure 2. Conversion (α) as a function of time for samples containing different loading (wt %) of ESO at the heating rate of 7.5 °C/min.

Table 1. Curing Characteristics of Samples Containing the Different Loadings of ESO

ESO (wt %)	heating rate (°C/min)	T_{onset} (°C)	T_{end} (°C)	T_{p} (°C)	ΔH_{total} (J/g)
10	2.5	129.95	208.30	149.88	189.60
	5	134.86	234.56	170.10	186.80
	7.5	137.37	226.14	176.86	189.39
	10	141.27	246.09	187.01	188.43
20	2.5	131.49	201.80	150.54	169.32
	5	135.38	229.27	168.95	164.37
	7.5	140.38	233.05	180.07	167.12
	10	143.06	234.79	189.71	169.06
30	2.5	131.54	203.57	157.55	160.38
	5	135.72	222.88	171.25	160.13
	7.5	138.18	254.45	180.99	159.76
	10	141.17	255.50	189.94	159.08

ESO in comparison with the main epoxy matrix leading to the lower reactivity of ESO in comparison with the DGEBA-based epoxy resin. The results revealed that the enthalpy of reaction and the maximum exothermic temperature for all samples is higher than the data related to epoxy cured with amine hardener³⁵ and lower than the results of the amino acid curing agent;⁸ it is close to the enthalpy of reaction of epoxy cured with difunctional benzoxazine.³⁶ As shown in Figure 2, there was a slight difference between the extent of curing of samples containing 10 wt % of ESO and the samples containing 20 and 30 wt % of ESO. The change in conversion of curing of samples containing 20 and 30 wt % of ESO is similar up to a high extent of curing. It is similar to the trend in the activation energy of reaction, which is discussed in the following paragraphs.

As described in the theory section, Friedman, Kissinger–Akahira–Sunose (KAS), and Starink methods were used to define the activation energy of samples containing 10, 20, and 30 wt % of ESO. In order to define the activation energy based on the Friedman method, $\ln(\beta d\alpha/dt)$ vs $1000/T$ was plotted for different samples in the conversion range of 0.05–0.95 with a step of 0.05. Figure 3 shows the Friedman plots for conversion in the range of 0.05–0.95 for samples containing 10 wt % of ESO. As shown in this figure, the data failed to fit a line due to low R^2 , and it seems that this method is not appropriate for the studied systems. This can be due to the sensitivity of the Friedman method in the determination of a baseline and the calibration of thermal analysis equipment.³⁷

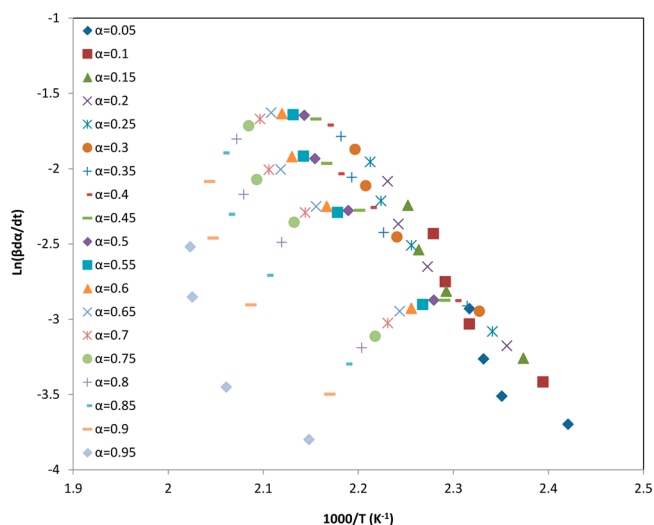


Figure 3. Friedman plot at different conversion degrees for epoxy containing 20 wt % of ESO.

In the next step, the KAS plots were plotted using $\ln(\beta/T^2)$ vs $1000/T$ in the conversion range of 0.05–0.95 with a step of 0.05. Figure 4 exhibits one example of the KAS plots for samples containing 20 wt % of ESO. Figure 5 shows the change in activation energy with degree of curing obtained from the KAS plots.

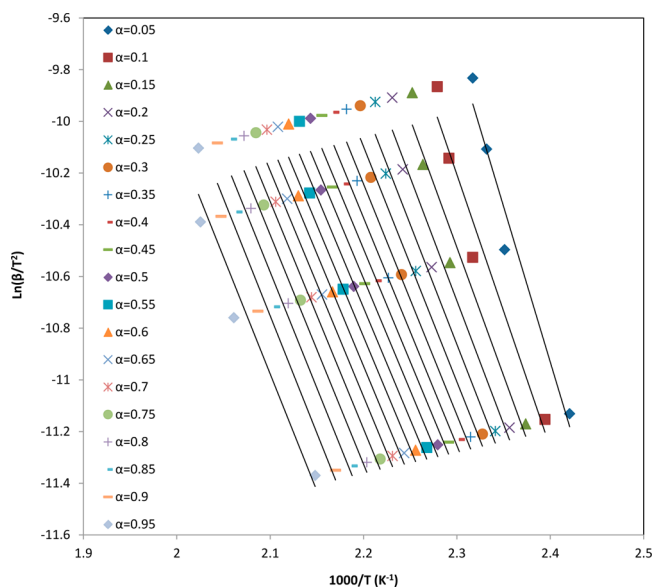


Figure 4. KAS plot at conversion degree between 0.05 and 0.95 for epoxy containing 20 wt % of ESO.

As shown in Figure 5, there is slight change in the activation energy of samples containing 10, 20, and 30 wt % of ESO with increasing the extent of curing at the early stage of curing (before 20% conversion). This dependence of activation energy on the conversion of reaction is known as the kinetic compensation effect.¹⁸ It can be found that the activation energy of samples containing 10 wt % of ESO decreased from 93.84 to 70.82 kJ mol^{-1} in the early stage of curing ($\alpha < 0.25$) and remained constant. This trend is followed also by the samples containing 20 wt % of ESO. The activation energy of this sample decreased from 100.05 to 75.62 KJmol^{-1} , and it

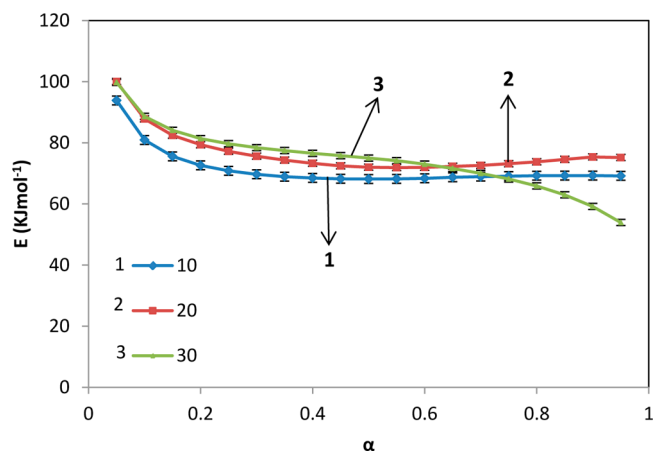


Figure 5. Variation of activation energy vs conversion for samples containing different loading (wt %) of ESO (KAS method).

remained constant at a higher extent of curing. This fast decrease in activation energy in the early stage of reaction is usually attributed to the change in the reaction mechanism from a noncatalyzed reaction to autocatalytic one due to the increase in concentration of hydroxyl groups.³⁸ A similar trend was also observed by Ferdosian et al. for different epoxy systems.³⁹ The samples containing 30 wt % of ESO showed a gradual decrease in activation energy for conversion greater than 0.85, which can be attributed to the change in the rate-determining step from a chemical-controlled to diffusion-controlled process. It must be recognized that the rate of a chemical reaction in any medium other than the vacuum is dependent on the rate of diffusion of reactant, and this becomes a more significant factor when the motion of reactant molecules is impeded due to the increase in viscosity of the system as the polymer change increases. In this situation, a small molecule can react when it reaches other reactant groups after some diffusion jumps.³⁵ It is also easily shown that the activation energy of samples containing 10 wt % of ESO is lower than the activation energy of other counterparts confirming the results shown in Table 1. This decreasing trend was observed with different researchers for various studied systems at the final stage of curing.^{16,17}

As mentioned in the Experimental Section, the Starink method is one of the most suggested isoconversional methods. Figure 6 shows the plot for epoxy containing 20 wt % of ESO cured with sebacic acid in the range of 0.05–0.95 conversion as an example. As shown in eq 7, the slope of line fitted on the curve of $\ln(\beta/T^{1.92})$ vs $1000/T$ can give the activation energy of system. Figure 7 shows the change in activation energy of the studied systems with a degree of curing. As shown in figure, the change in activation energy is similar to the results obtained from the KAS method. It should be noted that the activation energy obtained from this method is very similar to that obtained from the KAS method.

Figure 8 shows the change in the glass transition temperature of cured samples containing different amounts of ESO. As shown in the figure, at a constant curing temperature, the glass transition temperature decreased as the amount of ESO increased. It is also found that the glass transition temperatures of samples cured at higher temperatures are greater than their counterparts cured at lower temperatures. This can be easily attributed to the lower extent of curing of samples and the lower cross-link density of samples cured at lower temperatures.

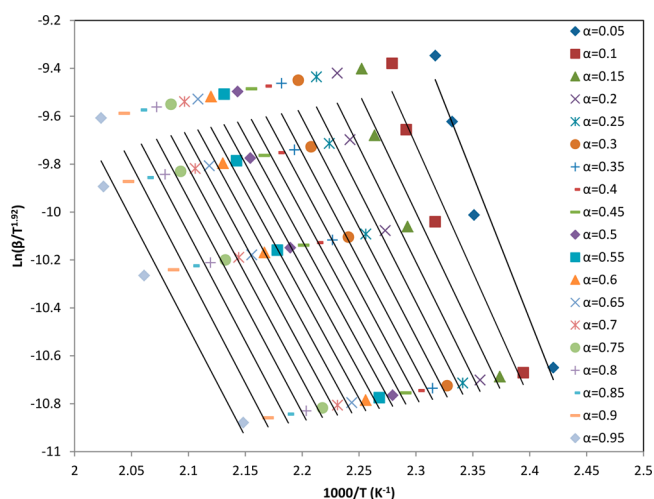


Figure 6. Starink plot at different conversion degrees for epoxy containing 20 wt % of ESO.

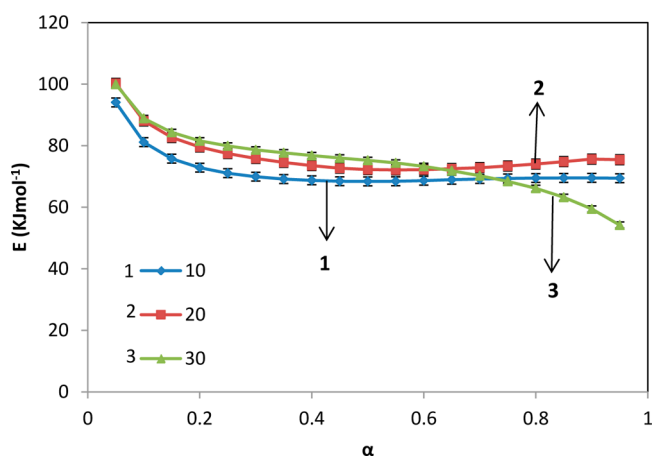


Figure 7. Variation of activation energy vs conversion for samples containing different loading (wt %) of ESO (Starink method).

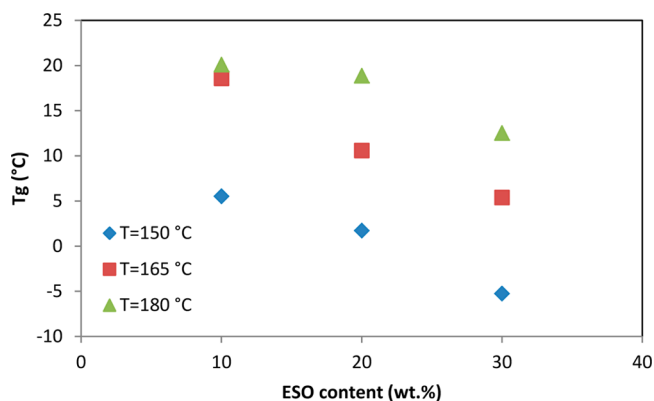


Figure 8. Glass transition temperatures of cured samples at different temperatures containing various loadings of ESO.

This trend is also observed by Miyagawa et al. for samples containing epoxidized linseed oil.^{1,2} It was observed that the glass transition temperatures of studied samples were lower than the samples cured with anhydride or amine,^{40,41} which usually vary in the range of 80–220 °C based on the hardener chemical structure. This can be easily attributed to the lower

cross-link density of the studied cured system and the difference in their chemical structures.

CONCLUSION

The kinetics of the curing reaction of a biobased thermoset system, i.e., an epoxy resin cured with a novel biobased hardener and containing different amounts of ESO (10, 20, and 30 wt %), was investigated in this study with nonisothermal DSC measurements. The extent of curing as a function of time and temperature was obtained. Three different isoconversional methods (i.e., Friedman, Kissinger–Akahira–Sunose (KAS), and Starink) were used as powerful tools in order to determine the activation energy of these systems. The results showed that the curing reaction in the early stages is autocatalytic due to hydroxyl group formation during the reaction. It was observed that the addition of different amounts of epoxidized soybean oil can change the kinetics of curing. The samples containing 10 and 20 wt % of ESO showed the same trend in the change of activation energy with conversion (i.e., decrease in activation energy in early stages of curing followed by constant activation energy), while the sample containing 30 wt % of ESO showed a different trend (i.e., decrease in activation energy at final stage of curing). In addition, it was found that the higher the amount of ESO, the higher the activation energy of reaction. It was found that the curing reaction of the sample containing 30 wt % of ESO was diffusion controlled at the final stage of curing. It was also found that the activation energy of the curing reaction of epoxy with biobased acidic hardener is higher than the common amine-based hardener, although it is lower than amino acid-based hardeners, which is an indication of a slower reaction of the studied system in comparison with amine hardeners and a higher curing rate than amino acid-based hardeners.

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Notes

The authors declare no competing financial interest.

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