

Cure Characterization of Soybean Oil—Styrene—Divinylbenzene Thermosetting Copolymers

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ABSTRACT: Bio-based resins are an alternative to petroleum-based resins in the production of fiber-reinforced polymers (FRPs) by processes such as pultrusion. A detailed understanding of the cure behavior of the resin is essential to determine the process variables for production of FRPs. In this work, the cure kinetics of soybean oil-styrene-divinylbenzene thermosetting polymers is characterized by differential scanning calorimetry (DSC) measurements. By varying the concentration of the cationic initiator from 1 to 3 weight

percent (wt %), the most viable resin composition for pultrusion is identified. The ability of phenomenological reaction models to describe the DSC measurements for the optimum resin composition is tested and kinetic equations, which can be used to determine the degree of cure at any temperature and time, are determined. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1042–1049, 2009

Key words: soybean oil; thermosets; DSC; cure kinetics

INTRODUCTION

Fiber-reinforced polymers (FRPs) are of significant interest in structural and engineering applications due to their excellent physical and mechanical properties. The applications of FRPs are often limited due to the high cost of the petroleum-based resins which constitute the polymer matrix.^{1,2} Bio-based resins offer an attractive alternative to petroleum-based resins, since they incorporate materials from renewable resources and may be manufactured at a lower cost. Furthermore, bio-based resins also have the potential to enhance the profitability of global agriculture, reduce reliance on diminishing fossil fuels for polymers, and mitigate the impact of petroleum-based polymers on the environment. The feasibility of producing resins from vegetable oils has been investigated by several researchers,^{3–13} since vegetable oils are characterized by a high degree of unsaturation and can form a cross-linked polymer network.³ Bio-based resins have been synthesized from biological oils by various methods, such as cationic polymerization,^{4–9} free radical polymerization,^{10–12} and ring opening metathesis polymerization.¹³ Larock and coworker^{5–9} have successfully synthesized a wide range of bio-resins through cationic copolymerization of biological oils with vinyl

monomers, such as styrene and divinylbenzene (DVB). In recent work,¹⁴ fiberglass composites using soybean oil-based resins from cationic polymerization have been produced and the mechanical properties of these materials were found to be comparable to those of petroleum-based FRPs.

FRPs are often manufactured by a process known as pultrusion in which fiber reinforcements are wetted with a polymer resin and continuously pulled through a die maintained at the required temperature.^{1,15} Accurate prediction and characterization of the cure behavior of resins to be employed in pultrusion is essential, since the cure kinetics of the resin has a direct impact on process variables, such as die temperature, pull speed, die length, and fiber content.¹⁶ Differential scanning calorimetry (DSC) measurements can be employed to obtain a detailed picture of the cure behavior for the resin.¹⁷ The cure kinetics of a resin can be studied either through isothermal measurements, which involve maintaining the sample at a fixed temperature for various intervals of time, or through dynamic measurements, which involve heating the sample at a constant rate over a given temperature range. In DSC measurements, the conversion (α) during cure ranges from 0 (completely uncured) to 1 (fully cured) and is defined as follows:

$$\alpha(t) = \frac{H(t)}{H_R} \quad (1)$$

where, $H(t)$ is the enthalpy of the reaction up to time t and H_R refers to the total heat of the reaction.

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TABLE I
Phenomenological Reaction Models used in This Work

Model	Designation	$f(\alpha)$	Parameters
n th Order	Fn	$(1 - \alpha)^n$	A, E_a, n
n th Order autocatalytic	FnA	$(1 - \alpha)^n(1 + K_{cat}\alpha)$	A, E_a, n, K_{cat}
Prout-Tompkins autocatalytic	PT	$(1 - \alpha)^n\alpha^m$	A, E_a, n, m

Typical DSC measurements involve measurement of the heat flow as a function of time and the enthalpy can be obtained by integration of the heat flow.

The kinetic parameters of the curing reaction can be obtained by fitting data obtained from DSC measurements using phenomenological reaction models. The cure rate or the evolution of conversion with time can be described as shown below:

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

where, $f(\alpha)$ refers to the reaction model, and $K(T)$ is the temperature dependent rate constant, which is defined through an Arrhenius relationship as follows:

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

where, A is the pre-exponential constant, E_a is the activation energy, R is the universal gas constant, and T is the absolute temperature. Dynamic DSC measurements can be described substituting $\beta = dT/dt$ in eq. (2), as shown below:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (4)$$

Hence, if the reaction model which describes the data is known, the conversion obtained at a given temperature or heating rate can be predicted using eqs. (2) and (4).^{18,19} Typically, the cure behavior of thermosetting resins is described by n th order or autocatalytic models, which are shown in Table I.

The objective of this work is to characterize the cure behavior of soybean oil-styrene-DVB thermosetting copolymer resins using DSC measurements since an understanding of the resin cure behavior and the kinetic parameters can facilitate development and optimization of cure schedules for processes such as pultrusion. The chemical structures of soybean oil, styrene, and DVB are represented in Figure 1. Soybean oil has ~ 4.5 carbon-carbon double bonds per triglyceride, which facilitates the formation of a cross-linked network. DVB acts as the cross-linking agent and incorporation of styrene promotes uniform cross-linking in these resins.⁵ Li and Larock⁵ have reported that the cationic polymerization of the monomers soybean oil, styrene, and DVB

in the presence of boron trifluoride diethyl etherate (BFE) initiator is heterogeneous due to differences in miscibility between the soybean oil and the BFE. Hence, understanding the impact of the initiator concentration on the polymerization reaction kinetics is essential. In this work, the impact of the cationic initiator on the cure kinetics of the resin and the dynamic mechanical properties of the resulting polymers will be studied by using three different BFE initiator concentrations of 1, 2, and 3 weight percent (wt %). The upper limit of BFE initiator concentration was chosen to be 3% since previous work⁵ with LoSatSoy oil indicated a decrease in the yield of cross-linked polymer and the gel time at higher concentrations. The experimental results are used to identify the optimum resin composition for pultrusion. The ability of phenomenological reaction models to describe the cure behavior of the resin is tested and kinetic equations, which can be used to predict the degree of cure at any temperature, are developed.

EXPERIMENTAL

Materials

The soybean oil used in this study was food grade and purchased from a local supermarket. Styrene (ST, 99%), DVB (80% mixture of isomers), and BFE (redistilled) were purchased from Aldrich Chemical Company and used without further purification. The monomer compositions for the three different initiator concentrations are tabulated in Table II.

DSC measurements

DSC measurements were performed using a model Q20 DSC from TA Instruments (New Castle, DE). The experiments were performed under a constant nitrogen flow of 50 mL/min. The specified wt % of soybean oil, styrene, and DVB corresponding to each initiator concentration (Table II) were added to a vial under stirring and the vial was cooled prior to initiator addition. The desired amount of the initiator was added at ambient temperature ($\approx 22^\circ\text{C}$) to the cooled solution and was mixed at 1200 rpm using a magnetic stir bar. The vial was immediately flash frozen under liquid nitrogen to prevent premature curing reactions before the measurements. Prior

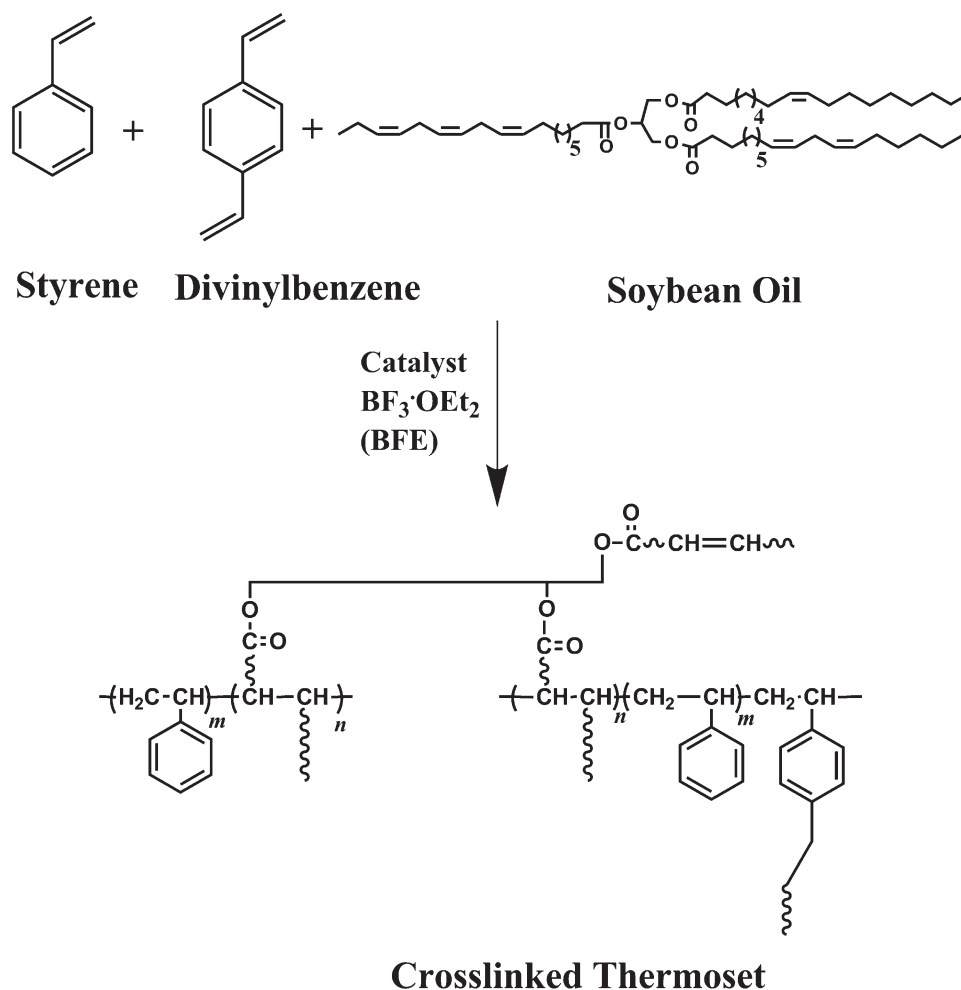


Figure 1 Structures of styrene, divinylbenzene, soybean oil, and the cross-linked thermoset obtained through cationic polymerization in the presence of a boron trifluoride diethyl etherate (BFE) initiator.

to the dynamic DSC experiments, the vial was partly defrosted and a small amount of sample (7–9 mg) was transferred to a hermetic aluminum DSC pan. The sample pan was placed in the DSC cell at a standby temperature of -30°C . The samples were heated from -30 to 220°C at rates of 25, 20, 15, and 10 K/min, for each initiator concentration.

Isothermal measurements were performed only for the optimum resin composition for pultrusion. The cure behavior of the optimum resin composition was examined at temperatures of 120, 140, and 160°C . For the isothermal measurements, the mixture of monomers and the initiator was poured into a silicone mold and placed in a convection oven maintained at the required temperature. The sample was allowed to cure at the specified temperature for various times ranging from 1 to 8 min. After each cure cycle, the mold was removed from the oven and immediately transferred to a liquid nitrogen bath to prevent further cure. A small piece (7–9 mg) of the sample was transferred to a standard DSC pan and placed in the DSC cell maintained at -30°C . The

sample was heated from -30 to 300°C at 10 K/min to measure the residual heat of the reaction (ΔH_R). The conversion for the partly cured sample was calculated using the residual heat of the reaction and the total heat of the reaction for the uncured sample measured at 10 K/min.

DMA measurements

The dynamic mechanical properties of the specimens were determined using a dynamic mechanical analyzer (TA instruments DMA Q800). The samples for

TABLE II
Composition of the Soybean Oil-Styrene-Divinylbenzene Thermosetting Resin

Initiator (wt %)	Soybean oil (wt %)	Styrene (wt %)	Divinylbenzene (wt %)
1	51	25.5	22.5
2	50	25	23
3	50	25	22

DMA measurements were prepared by placing a mold containing the liquid monomers in a hot press at 110°C for 10 min under 3000 psi; subsequently, the samples were postcured at 110°C in a convection oven under atmosphere pressure for 10 h. Fully cured specimens with a typical size of about 15.0 mm × 7.0 mm (length × width) were used for the measurements. The measurements were performed in the three point bending mode at a frequency of 1 Hz. The dynamic properties were measured on heating at a rate of 5°C/min from -60 to 200°C.

RESULTS AND DISCUSSION

The DSC curves obtained on heating at various rates from 10 to 25 K/min for the three thermosetting resin systems are shown in Figure 2(a-c). For all the compositions, the magnitude of the reaction exotherm increases with increasing heating rate, as expected. The kinetic parameters of the cure can be determined from dynamic DSC measurements using Kissinger's equation as follows:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \quad (5)$$

where, T_p is the peak temperature of the cure exotherm, which increases with increasing heating rate. The parameters E_a and A can be determined from a plot of $\ln\left(\frac{\beta}{T_p^2}\right)$ versus $\frac{1}{T_p}$, as shown in Figure 3, for the three thermosetting resins. The values of E_a and $\ln A$ are tabulated as a function of initiator concentration in Table III. The overall activation energy of the cure is found to decrease with increasing initiator concentration.

The onset of the cure exotherm shifts to lower temperatures with increasing initiator concentration, as demonstrated in Figure 4 for a heating rate of 10 K/min. From Figure 4, it is clear that unlike the resin with 1 wt % initiator, the thermosetting resins with 2 and 3 wt % initiators are characterized by the presence of a second exotherm at 160 and 150°C, respectively. The second exotherm in the resins with 2 and 3 wt % initiator concentrations could be due to additional reactions of the triglycerides in the soybean oil which results in a complex cure behavior for these resins. The additional reactions might be a consequence of the heterogeneous nature of the reactions due to differences in miscibility between the oil and the BFE. However, the concentration of initiator might not be sufficient for the additional reaction to occur in the 1 wt % initiator system. Most importantly, Figure 4 also indicates that the thermosetting resin with 3 wt % initiator concentration might not be suited for processing by traditional pultrusion methods, since the resin starts to cure at

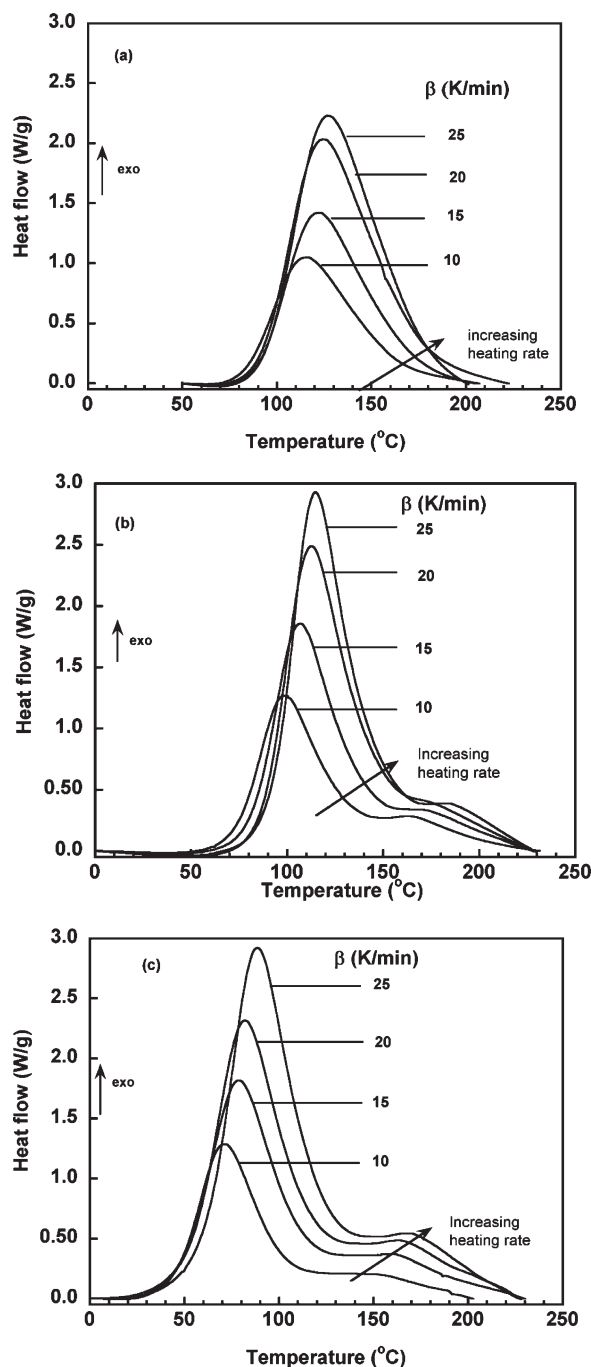


Figure 2 Dynamic DSC measurements of the cure behavior for soybeanoil-styrene-divinylbenzene thermosetting copolymers (a) 1 wt % BFE. (b) 2 wt % BFE. (c) 3 wt % BFE.

room temperature, which may lead to premature gelation prior to processing.

To identify the optimum resin composition, the results from DMA measurements are compared in Figure 5. The loss factor ($\tan \delta$), which is the ratio of the dynamic loss modulus (E'') and the storage modulus (E'), exhibits two distinct peaks at each initiator concentration. The low-temperature peak corresponds to the glass transition of the oil-rich phase

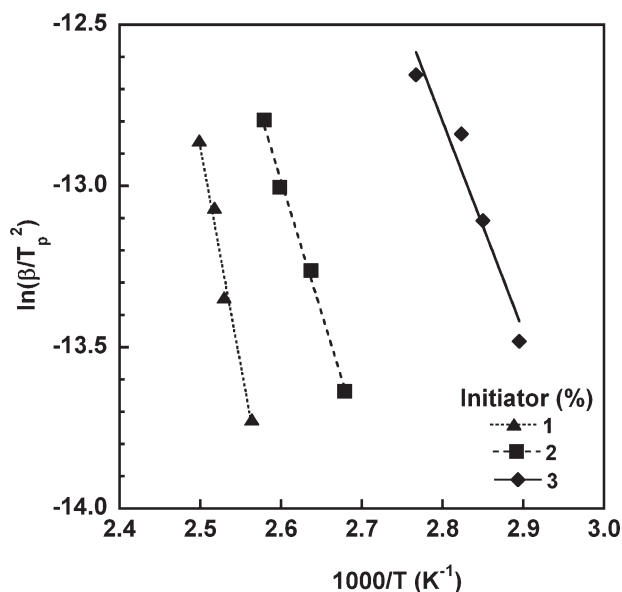


Figure 3 Determination of activation energy (E_a) as a function of initiator concentration from Kissinger's approach. E_a is determined from the slope of the best fit lines shown in the figure.

and the high-temperature peak corresponds to the glass transition of the styrene-rich phase. Hence, the occurrence of phase separation in the cross-linked network does not facilitate a comparison of the glass transition temperatures (T_{gs}) for the thermosetting resins from the loss factor curves. However, based on the DMA measurements, the dynamic storage modulus is found to increase with increasing initiator concentration, as shown in Figure 5. The room temperature modulus of the resin with 2 wt % initiator (0.35 GPa) is found to be 30% higher than the corresponding value for the resin with 1 wt % initiator (0.27 GPa). Hence, the resin with 2 wt % BFE initiators is identified as the best choice for pultrusion, since it exhibits better mechanical properties than the resin with 1 wt % initiator and better latency than the resin with 3 wt % BFE, which begins to cure at room temperature.

The dynamic DSC measurements of the resins were fit with reaction models shown in Table I, to determine the model which provides the best description of the cure behavior. The model parameters and F -values are tabulated in Table IV. The

TABLE III
Determination of Kinetic Parameters from Dynamic DSC Measurements Using Kissinger's Equation

Initiator (wt %)	E_a (kJ/mol)	$\ln(A)$
1	113 ± 10	24 ± 3
2	68 ± 3	10 ± 1
3	54 ± 9	7 ± 3

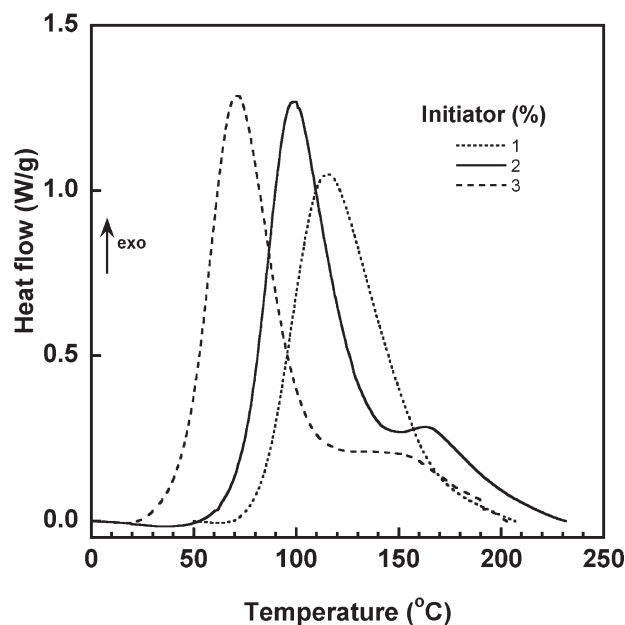


Figure 4 Comparison of cure kinetics of the resins with different concentrations of boron trifluoride diethyl etherate (BFE) initiator.

F -values are obtained from a statistical F -test, which determines the best model fit by comparing the residual variances of the individual model fits. The resin with 1 wt % BFE is equally well-described by the n th order model and autocatalytic models, since the F -values are found to be the same. However, the resins with 2 and 3 wt % BFE are better described by autocatalytic models. In particular, for the resin with 2 wt % BFE, which is the optimum

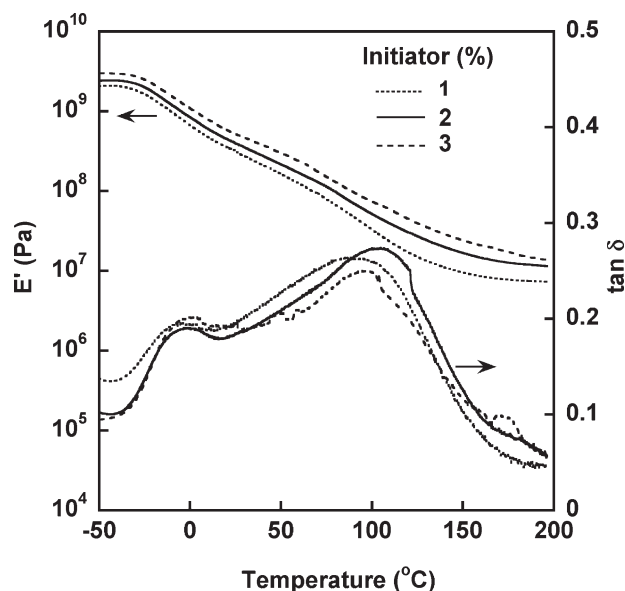


Figure 5 Variation of dynamic mechanical properties as a function of the initiator concentration from DMA measurements.

TABLE IV
Model Parameters Determined by Fitting Dynamic DSC Measurements with Phenomenological Reaction Models

Initiator (wt %)	Model	E_a (kJ/mol)	$\log A$ (s^{-1})	n	$\log K_{cat}$	m	F -value ^a
1	Fn	114.11	13.34	2.61			1.00
	FnA	113.99	13.33	2.61	-4		1.00
	PT	108.55	12.62	2.56		0.006	1.00
2	Fn	151.27	19.12	4.0			2.63
	FnA	67.34	6.55	3.4	1.50		1.21
	PT	64.38	7.41	3.0		0.61	1.00
3	Fn	108.5	14.4	4.46			1.09
	FnA	50.1	4.73	3.85	1.4		1.00
	PT	47.36	5.56	3.40		0.60	1.17

^a The critical F -value at 95% confidence interval is 1.09.

composition, the Prout-Tompkins autocatalytic model is found to provide the best description of the data, since the F -value is lower than the critical F -value at 95% confidence only for this model. However, as shown in Figure 6, significant deviations between the model calculations and the experimental results can be observed, especially at higher temperatures, where the second exotherm occurs. The variation of activation energy during the cure for the resin with 2 wt % initiator was determined by performing an isoconversional analysis, as shown below:

$$\log \beta = \frac{-0.4567 \cdot E_a}{R \cdot T_i} + A' \quad (6)$$

The activation energies obtained as the slope of a plot of $\log \beta$ versus $1/T$ for different temperatures are plotted as a function of the degree of cure in Figure 7.

The errors in the activation energies are found to be between 30 and 50% at higher conversion (>80%). However, Figure 7 clearly demonstrates the lack of autocatalytic kinetics for this resin, since no decrease in activation energy can be observed in the initial stages of the cure; this discrepancy between model predictions and experiments is due to the inability of the phenomenological models to adequately describe the complex cure behavior observed in the dynamic DSC measurements of the resins.

Characterization and prediction of the reaction kinetics at high temperatures which correspond to a high degree of cure, is crucial for pultrusion. Consequently, the cure kinetics of the optimum composition (2 wt % initiator) was further characterized by isothermal cure measurements. The values of ΔH_R for each cure cycle and the value of the total

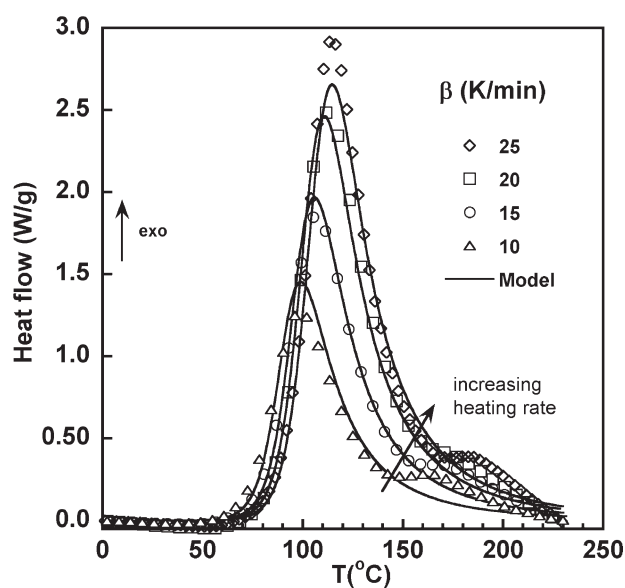


Figure 6 Comparison between dynamic DSC experiments and model calculations from Prout-Tompkins autocatalytic model for the thermoset with 2 wt % initiator. The model calculations are shown as the solid lines and the experimental data are represented by solid symbols.

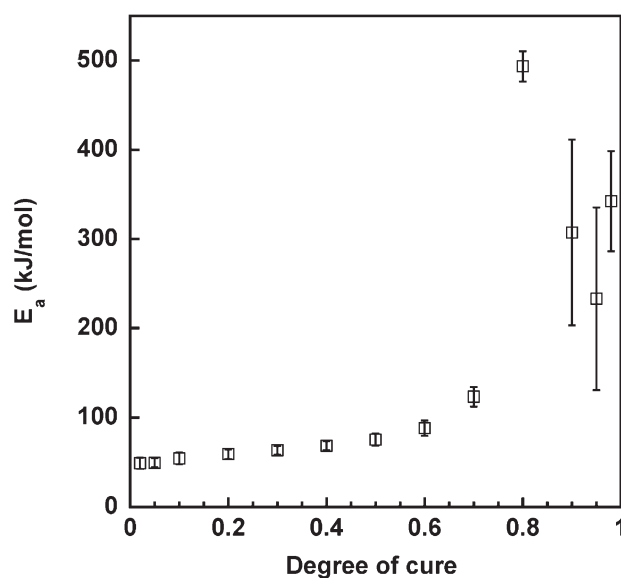


Figure 7 Variation of activation energy with degree of cure by isoconversion analysis for the resin with 2% BFE. The values of E_a were determined from a plot of $\log \beta$ versus $1/T$ at different temperatures.

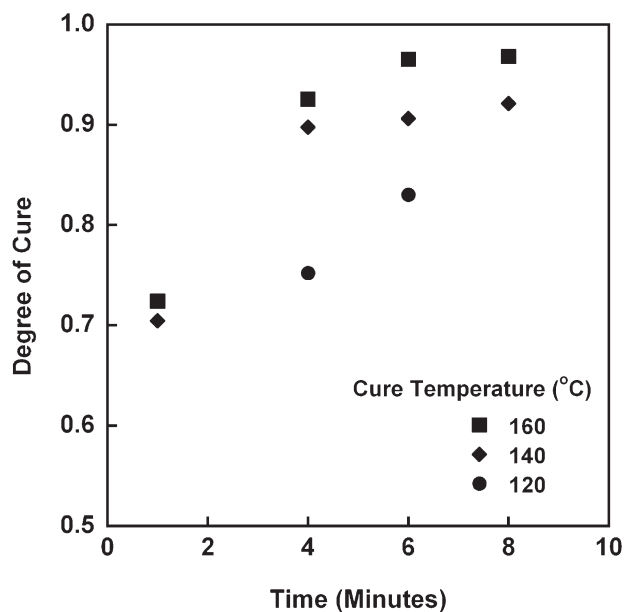


Figure 8 Degree of cure as a function of time at various isothermal cure temperatures.

enthalpy of reaction (ΔH_T) measured at 10 K/min were used to compute the degree of cure as shown below:

$$\alpha = \frac{\Delta H_T - \Delta H_R}{\Delta H_T} \quad (7)$$

The degree of cure attained on curing at different temperatures for various times are shown in Figure 8. For the same cure time, the degree of cure increases with increasing temperature, as expected. The resin cures rapidly and attains a cure of 93% for a cure time of 4 min at a cure temperature of 160°C, which reiterates the fact that the resin is ideally suited for production of FRPs through pultrusion.

The data obtained in Figure 8 can be used to form a master curve by shifting the cure time (t_1) at a temperature of interest (T_1) with respect to a reference temperature ($T_{\text{ref}} = 160^\circ\text{C}$) as shown below²⁰:

$$t_{\text{ref}} = t_1 \exp \left[\frac{E_a(T_1 - T_{\text{ref}})}{RT_1 T_{\text{ref}}} \right] \quad (8)$$

where, the value of E_a was found to be 68 kJ/mol based on Kissinger's approach (Table III). The master curve can be well described using an n th order reaction model, as shown in Figure 9. The best fit parameters ($n = 2.4$ and $K_{160} = 7.3 \text{ min}^{-1}$) can be used to determine the kinetic equation for the cure, as shown below:

$$\frac{d\alpha}{dt} = K(T)(1 - \alpha)^n \quad (9)$$

integration of eq. (9) yields the equation for conversion at 160°C.

$$\begin{aligned} \alpha_{160^\circ\text{C}} &= 1 - (1.4K_{160} t + 1)^{-(n-1)^{-1}} \\ &= 1 - (10.2t + 1)^{-0.71} \quad (10) \end{aligned}$$

The rate constant at any temperature can be determined as shown in eq. (11):

$$K(T) = K_{160} \exp \left[\frac{E_a(T - 160)}{R(160 + 273)T} \right] \quad (11)$$

Hence, from eqs. (9)–(11), the master curve of conversion versus time for any cure temperature can be obtained.²⁰

CONCLUSIONS

The cure kinetics of soybean oil-styrene-DVB thermosetting copolymers has been examined by DSC measurements. The concentration of the cationic initiator had a significant impact on the cure kinetics and the mechanical properties of the resin. The resin with 2 wt % BFE was identified as a viable choice for production of FRPs by pultrusion due to its better mechanical properties compared with the resin with 1 wt % BFE and due to the low onset cure temperature of the resin with 3 wt % BFE. Autocatalytic reaction models were able to provide a good description of the dynamic DSC data for the resin with 2 wt % BFE, but significant deviations were observed at high temperatures; however, the master curve of isothermal cure measurements for the resin was well-described by an n th order model. Kinetic

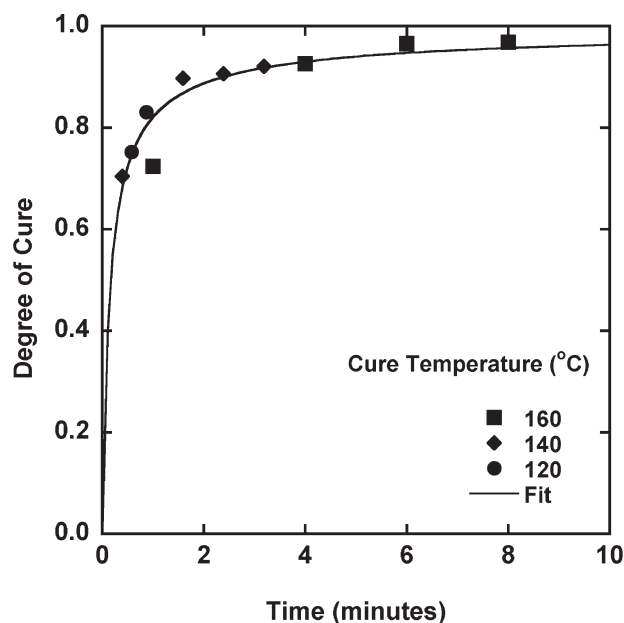


Figure 9 Master curve obtained by shifting the data to a reference temperature of 160°C. The solid line represents the best fit to the data using an n th order model.

equations necessary to predict the degree of cure at any cure temperature have been determined.

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