

Process Feasibility and Kinetic Analysis of Glass Fiber-Reinforced Vinyl Ester/Nano-Al₂O₃ Matrix Composites for Pultrusion

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ABSTRACT: This work presents a process developed to manufacture glass fiber-reinforced vinyl ester (VE)/nano-Al₂O₃ matrix composites by pultrusion method. The matrix prepolymer for pultrusion in this study was prepared from blends of VE, initiator (*t*-butyl perbenzoate), and nano-Al₂O₃. The process feasibility and kinetic analysis of the unidirectional glass fiber-reinforced VE/nano-Al₂O₃ matrix composites by pultrusion have been investigated. From the investigations of the long pot life of VE/nano-Al₂O₃ matrix, the high reactivity of VE/nano-Al₂O₃ matrix, and excellent fiber wet-out of VE/nano-Al₂O₃ matrix and glass fiber, it

was found that the VE/nano-Al₂O₃ matrix showed excellent process feasibility for pultrusion. A kinetic autocatalytic model, $d\alpha/dt = A \exp(-E/RT)\alpha^m(1 - \alpha)^n$, was proposed to describe the curing behavior of glass fiber-reinforced VE/nano-Al₂O₃ matrix composites. Kinetic parameters for the model were obtained from dynamic differential scanning calorimetry scans using a multiple regression technique. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: E429–E434, 2012

Key words: vinyl ester; nano-Al₂O₃; pultrusion; composites; process feasibility; kinetics

INTRODUCTION

Pultrusion is an automatic process for producing continuous and constant cross-sectional profile composite materials.^{1,2} It can produce composites of almost unlimited length with more flexibility and higher tensile strength than any other process.^{3,4} This process has emerged as one of the most cost-effective processing techniques for composites. It is the fastest growing manufacturing processes of polymer matrix composites.⁵ The methods of manufacturing pultruded products include the emulsion pultrusion,⁶ hot melt pultrusion,⁷ fluidized bed pultrusion,⁸ slurry pultrusion,⁹ *in situ* polymerization pultrusion,¹⁰ reaction injection pultrusion,^{11–13} and matrix fiber interwoven with reinforced fiber prepregs pultrusion.¹⁴ Except for *in situ* polymerization, other methods create poor fiber wet-out and serious shrinkage of pultruded products. Therefore, *in situ* polymerization for pultrusion is the best method to manufacture pultruded composites. Figure 1 shows a schematic

representation of the *in situ* polymerization pultrusion process.

Generally, the process feasibility of matrix for an *in situ* polymerization pultrusion process must meet the following criteria: (1) a suitable viscosity (400–2000 mPa s) in the impregnation tank, (2) a long pot life in the impregnation tank, (3) high reactivity in the die, and (4) good wetting ability between fiber and resin.^{15,16} The fiber will exhibit excellent wet-out when the resin has a suitable viscosity in the impregnation tank. Long pot life in the impregnation tank means that the viscosity of resin should only increase slightly over long processing time; hence, the fibers have adequate time to be wetted out, and the pultrusion process can be operated for a long time. To fabricate the composites in a short time in the pultrusion die, the resin should have high reactivity. Furthermore, good fiber wet-out should be obtained to reach the optimum mechanical properties for the composites. We want to study the curing reaction of composites for pultrusion process. The technique of dynamic differential scanning calorimetry (DSC) has been found to provide a useful method to monitor the course of exothermic cure reactions.^{17,18} Using this method, the kinetic model and kinetic parameters of resin can be obtained from simulation under nonisothermal conditions.

Formerly, no one has ever done this kind of research about resin/nano-Al₂O₃ matrix for pultrusion;

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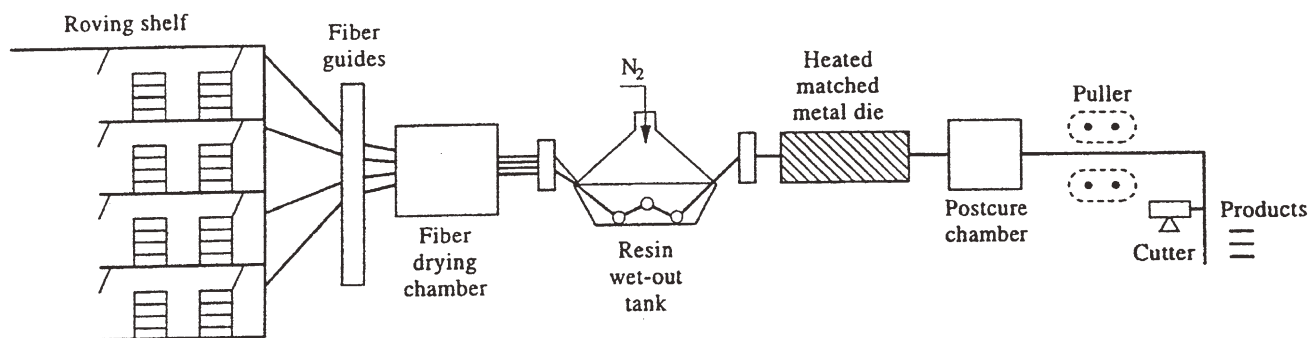


Figure 1 Flow chart of *in situ* pultrusion machine.

therefore, this work is very heavy for pultrusion processes. The vinyl ester (VE) resin shows the characteristics of long pot life, high reactivity, and good glass fiber wet-out, and it is suitable for the pultrusion process. The nano- Al_2O_3 has unique properties that included high strength, high modulus, high conductivity, low-thermal expanded coefficient, thermal impact resistance, high chemical stability, high electric insulation, high acid, alkalinity, and solvent resistance,¹⁹ and it can increase the properties of the pultruded VE composites. Hence, this work investigates a proprietary process to manufacture glass fiber-reinforced VE/nano- Al_2O_3 composites by pultrusion. In this study, using the VE/nano- Al_2O_3 and glass fiber treated as the matrix and reinforcements for pultrusion process. The matrix was used directly and polymerized in the pultrusion die by controlling the viscosity of matrix and the self-designed pultrusion facility. It provides a new concept for *in situ* polymerization pultrusion. This study investigates the process feasibility and kinetic analysis of glass fiber-reinforced VE/nano- Al_2O_3 matrix composites by *in situ* polymerization pultrusion method.

EXPERIMENTAL

Materials

The VE prepolymer used was bisphenol-A type and was supplied by the Swancor Co., Taiwan, ROC; it has a viscosity of 350 mPa s at 25°C, and its chemical structure is described in Figure 2. The initiator used was *t*-butyl perbenzoate (TBPB) and was supplied from the Chiangya Co., Taiwan, ROC; it has a density of 1040 kg/m³, a molecular weight of 194, and a viscosity of 6 mPa s at 25°C. The nano- Al_2O_3 particle

has a diameter of 38.2 nm; a specific surface area of 43.6 m²/g; a density of 3600 kg/m³. The continuous E-glass fiber roving was TGFR-P1200, which was obtained from the Taiwan Glass Industry Co., Taiwan, ROC; it has a filament diameter of 17 μm, a density of 2540 kg/m³, a tensile strength of 3500 MPa, an elastic modulus of 73 GPa, and an elongation of 4.8% at 25°C.

Preparation of VE/nano- Al_2O_3 matrix

The VE resin was prepared from the mixture of VE prepolymer with TBPB at weight ratio of 100/1. And the VE/nano- Al_2O_3 matrix was prepared by mixing VE resin with various nano- Al_2O_3 particles at 25–55°C. Complete mixing of the components was achieved using a high-torque stirrer.

Apparatus and measurement

The pultrusion machine was custom-designed. It consisted of multiple heating zones and a pultrusion die with dimensions of 0.82 × 0.0127 × 0.00319 m (length × width × thickness). The surfaces of the stainless steel die were treated by chrome plating. Viscosities of matrix were measured with a Brookfield RVF model viscometer (Brookfield Co., USA). Fourier transform infrared (FTIR) measurements were carried out with a Model FTIR-460 (Jasco Co., Japan). The sample was directly dabbed onto a KBr pellet for FTIR tests. The gel time was measured following the specification of ASTM 3532-76. Gel time is recorded as the time at which the material no longer has a tendency to form "strings" when probing. Gel time is recorded to the nearest 1 s. The hot plate was set at a precise temperature (procedure 140–190°C). Taking 1–2 g matrix on the hot plate, a tip of a

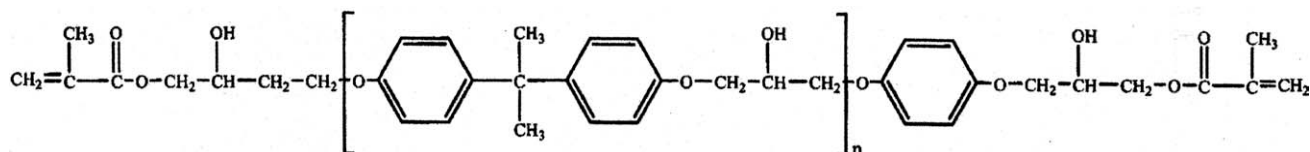


Figure 2 The chemical structure of vinyl ester (VE) prepolymer.

TABLE I
The Viscosity of VE/Nano- Al_2O_3 Matrix at 25°C

Al_2O_3 (phr)	Viscosity (mPa s)
0	332
1	462
2	540
3	620
4	702
5	1032
6	1603
7	2235

needle was used to pick the matrix three times per second, until the matrix was too sticky to be picked. The SEM photographs were obtained on a JSM-6335F scanning electron microscope (Jeol Co., Japan). The microphotographs were taken on the surface obtained by fracturing the specimen in liquid nitrogen and then coating it with gold powder. The flexural properties were measured on an Instron 1123 universal testing machine (Instron Co., USA) following the specification of ASTM D-790. The sample dimensions were $0.127 \times 0.0125 \times 0.003$ m (length \times width \times thickness), the span was 90 mm, and the crosshead speed was 2 mm/min. The sample dimensions were smaller than the dimensions of die, due to the sample shrinkage during processing. The notched Izod impact strength testing machine was a Gotech GT-7045 (Gotech Co., Taiwan) used in accordance with ASTM D-256. The sample dimensions were $0.0635 \times 0.0125 \times 0.003$ m (length \times width \times thickness), and the notch depth was 2.5 mm. The DSC used was a Model 2010, DuPont Co., USA.

RESULTS AND DISCUSSION

Process feasibility study

The VE/nano- Al_2O_3 matrix used for *in situ* pultrusion process must possess the following characteristics: (1) a suitable viscosity (400–2000 mPa s) in the impregnation tank; (2) long pot life in the impregnation tank; (3) high reactivity in the die; and (4) good wet-out between fiber and matrix.

Viscosity in the impregnation tank

As the suitable viscosity of VE/nano- Al_2O_3 matrix in the impregnation for pultrusion, process must be set at 400–2000 mPa s. Table I shows the viscosity of VE/nano- Al_2O_3 matrix at 25°C. When the nano- Al_2O_3 content of matrix exceeded 6 phr in matrix, its viscosity was higher than 2000 mPa s. Therefore, this matrix was not suitable to use in pultrusion process when the nano- Al_2O_3 content of matrix exceeded 6 phr. However, when the nano- Al_2O_3 content was exceeded 4 phr, the pultrusion process cannot proceed, because the process was jammed in the die. Therefore,

the optimum nano- Al_2O_3 content of matrix in the impregnation tank was 1–3 phr, and the optimum process temperature in the impregnation tank was 25°C.

Pot life

To provide a sufficient time for glass fiber wet-out and subsequent pultrusion process, the pot life of VE/nano- Al_2O_3 matrix must be prolonged. Figure 3 shows the viscosity versus reaction time of VE/nano- Al_2O_3 matrix at various temperatures. One can observe the viscosity of matrix with 3 phr nano- Al_2O_3 content rise only 40 mPa s (from 620 to 660 mPa s) after 3 h at 25°C. These results indicate that the pot life of VE/nano- Al_2O_3 matrix was longer than 3 h when the impregnation tank is set at 25°C, which provides a sufficient time for subsequent pultrusion process.

Reactivity

In the pultrusion process, the VE/nano- Al_2O_3 matrix must have high reactivity; otherwise, they cannot be fabricated in a short time in the die. When the glass fiber-reinforced VE/nano- Al_2O_3 matrix composites were reacted in pultrusion die, only the matrix is polymerized. Hence, the reactivity data are very near between matrix and matrix/glass fiber. Generally, the VE resin is polymerized, and the FTIR spectra show that the absorption peaks $\text{C}=\text{C}$ disappear at 1630 cm^{-1} . Figure 4 shows the FTIR spectra of VE resin before and after reaction. From this figure, one can observe that when the VE resin is polymerized at 160°C for 60 s, the absorption peak intensity of $\text{C}=\text{C}$ at 1630 cm^{-1} disappears clearly. Figure 5 shows the gel time of VE/nano- Al_2O_3 matrix at various temperatures. From the figure, it is found that the VE/nano- Al_2O_3 matrix has short gel time (<60 s) when the temperature is above 160°C. From the observations of Figures 4 and 5, the VE/nano- Al_2O_3 matrix shows high reactivity at elevated temperature;

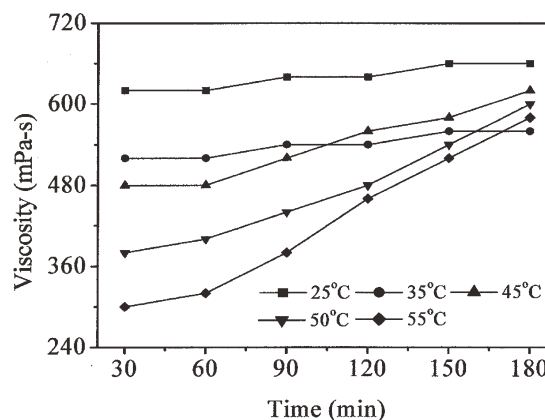


Figure 3 Viscosity versus time of VE/nano- Al_2O_3 matrix for 3 phr nano- Al_2O_3 content at various temperatures.

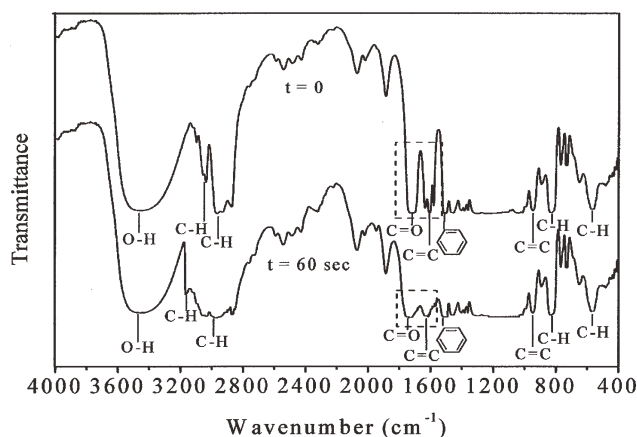


Figure 4 FTIR spectra of VE resin at reactive temperature of 160°C and time of 60 s.

thus, the composites can be fabricated in a short time in the pultrusion die.

Wetting ability of fiber

To obtain the best physical, mechanical, and thermal properties of pultruded composites, the excellent glass fiber wet-out is very important. The morphology phenomena can be observed by SEM photo-

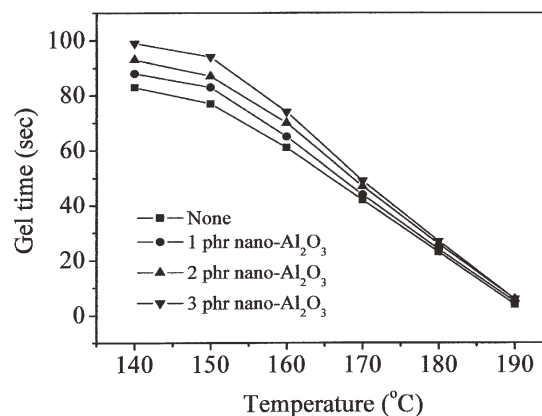


Figure 5 Effect of temperature on gel time of VE/nano-Al₂O₃ matrix.

graphs. The SEM destruct surface of pultruded unidirectional glass fiber-reinforced VE/nano-Al₂O₃ matrix composites is shown in Figure 6. From the destruct surface of Figure 6, it can be seen that the glass fiber surface still retains a lot of VE/nano-Al₂O₃ matrix after destruct tests. Therefore, excellent wet-out of glass fiber by VE/nano-Al₂O₃ matrix can be observed. Table II shows the mechanical properties (flexural strength, flexural modulus, and notched Izod impact strength) of pultruded unidirectional

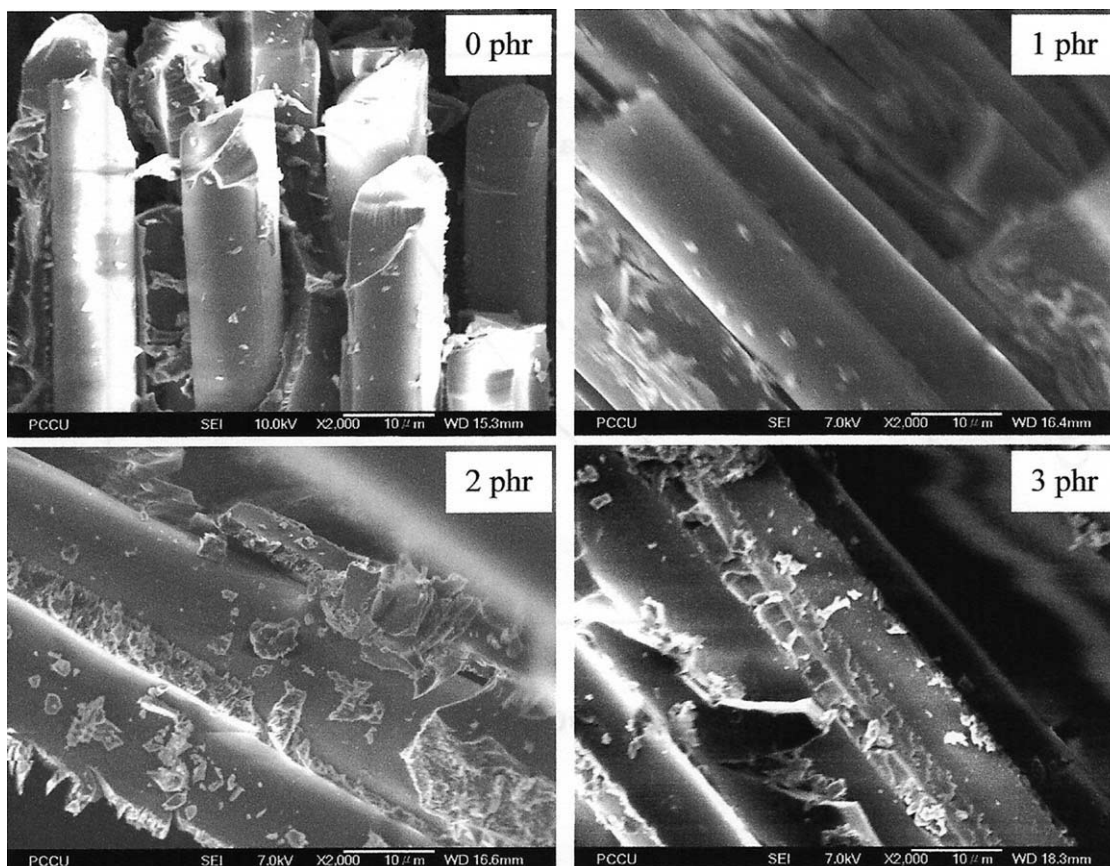


Figure 6 Destruct surfaces of SEM of pultruded glass fiber-reinforced VE/nano-Al₂O₃ matrix composites at various nano-Al₂O₃ content.

TABLE II
The Mechanical Properties of Pultruded Unidirectional Glass Fiber-Reinforced VE/Nano- Al_2O_3 Matrix Composites at Various Nano- Al_2O_3 Content

Al_2O_3 content (phr)	Flexural strength (MPa)	Flexural modulus (GPa)	Notched Izod impact strength (J/m)
0	850 ± 26.2	11.68 ± 0.32	4153 ± 123.6
1	997.1 ± 20.1	11.95 ± 0.48	4278 ± 98.4
2	1059.6 ± 42.2	14.90 ± 0.54	5071 ± 91.3
3	895.7 ± 22.4	14.52 ± 0.55	4267 ± 106.9

glass fiber-reinforced VE/nano- Al_2O_3 matrix composites at various nano- Al_2O_3 content. From this table, it can be seen that the mechanical properties of composites reach a maximum value at 2 phr nano- Al_2O_3 content and then decrease. The nano- Al_2O_3 content cannot be too high in pultruded composites; otherwise, the fiber wet-out will be wrong, because the viscosity of VE/nano- Al_2O_3 matrix is too high.

Kinetic analysis

The mechanistic kinetic model used in this study to describe the curing behavior of a glass fiber-reinforced VE/nano- Al_2O_3 matrix composites is based on an autocatalytic model. Details of the derivation are discussed elsewhere. The rate equation is given in eq. (1).¹⁰

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) \alpha^m (1-\alpha)^n \quad (1)$$

where α is the conversion (i.e., degree of curing), A is the pre-exponential factor, E is the activation energy, R is the universal gas constant, T is the absolute temperature, and m and n are the orders of reaction.

The heat evolved during the curing reaction and measured by the dynamic DSC thermogram at $10^\circ\text{C}/\text{min}$ can be related to the conversion (α) and conversion rate ($d\alpha/dt$) by

$$\Delta H = \int_0^t \frac{dQ_t}{dt} dt \quad (2)$$

$$\alpha = \frac{Q_t}{\Delta H} \quad (3)$$

TABLE III
Kinetic Parameters Are Obtained at Various Nano- Al_2O_3 Content of Matrix Using Autocatalytic Model

Nano- Al_2O_3 content (phr)	E (kJ/mol)	A (min^{-1})	m	n	$m+n$
1	81.69	2.85×10^5	0.603	1.489	2.092
2	90.76	3.16×10^5	0.659	1.417	2.076
3	80.92	2.79×10^5	0.634	1.462	2.096
Average	84.46	2.93×10^5	0.632	1.456	2.088

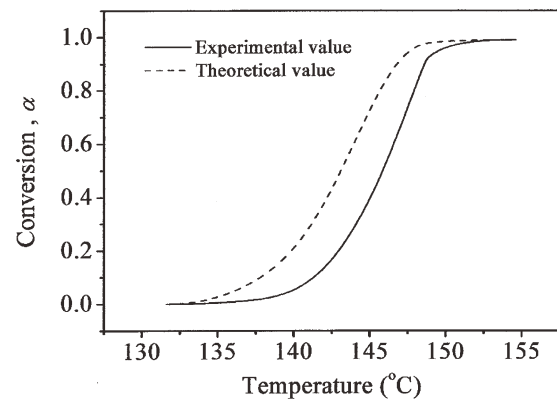


Figure 7 Conversion (α) versus temperature of composites for 1 phr nano- Al_2O_3 content from autocatalytic model theoretical value and experimental value by dynamic DSC at $10^\circ\text{C}/\text{min}$.

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H} \frac{dQ_t}{dt} \quad (4)$$

where α is the conversion at time t , Q_t is the reaction heat up to time t or temperature T , dQ_t/dt is the rate of heat evolution per unit mass of resin at time t , and ΔH is the total heat of reaction for 100% conversion. Equation (1) can be expressed in the logarithmic form as follows:

$$\ln \frac{d\alpha}{dt} = \ln A - \frac{E}{RT} + m \ln \alpha + n \ln(1-\alpha) \quad (5)$$

By integrating the DSC curve, the total reaction heat ΔH are 581.1, 433.6, and 249.5 J/g and can be obtained when the nano- Al_2O_3 content of matrix is set 1, 2, and 3 phr, respectively. First, we can choose 100 data of $(\frac{d\alpha}{dt}, \frac{1}{RT}, \alpha, 1-\alpha)$ from the dynamic $10^\circ\text{C}/\text{min}$ DSC experimental data and then make a logarithm to form 100 data of $[\ln \frac{d\alpha}{dt}, \frac{1}{RT}, \ln \alpha, \ln(1-\alpha)]$. Last, using a multiple regression technique

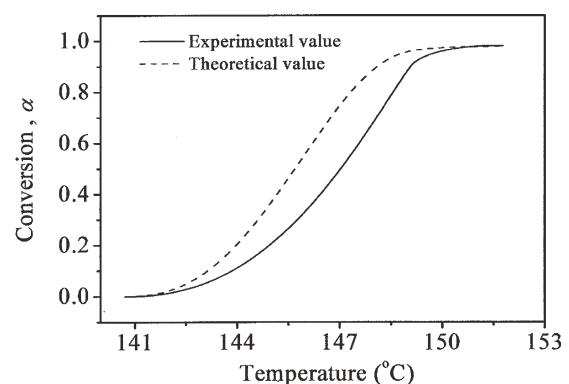


Figure 8 Conversion (α) versus temperature of composites for 2 phr nano- Al_2O_3 content from autocatalytic model theoretical value and experimental value by dynamic DSC at $10^\circ\text{C}/\text{min}$.

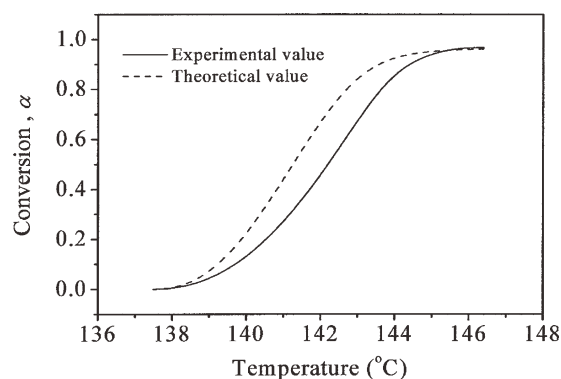


Figure 9 Conversion (α) versus temperature of composites for 3 phr nano- Al_2O_3 content from autocatalytic model theoretical value and experimental value by dynamic DSC at $10^\circ\text{C}/\text{min}$.

computation to solve eq. (5), one can obtain the kinetic parameters that include activation energy (E), pre-exponential factor (A), and reaction orders (m , n). The calculated kinetic parameters are listed in Table III. From this table, one can observe that the average kinetic parameters $E = 84.46$ kJ/mol, $A = 2.93 \times 10^5 \text{ min}^{-1}$, $m = 0.632$, $n = 1.456$, and total reactive orders $m + n = 2.088$. Figures 7–9 illustrate conversion (α) versus temperature of glass fiber-reinforced VE/nano- Al_2O_3 matrix composites from autocatalytic model theoretical value and experimental value by dynamic DSC at $10^\circ\text{C}/\text{min}$. The dashed lines represented the calculated theoretical value obtained from autocatalytic model of eq. (1) with the aforementioned kinetic parameters, whereas the solid lines are obtained directly from the DSC thermogram experimental value by using eqs. (3) and (4). From Figures 7–9 results, one can observe that the experimental value agrees very well with the theoretical prediction.

CONCLUSION

In this study, a suitable VE/nano- Al_2O_3 matrix system was developed for the pultrusion process. The process feasibility of the pultrusion of glass fiber-reinforced VE/nano- Al_2O_3 matrix composites has been demonstrated. From the viscosity study, the optimum temperature of VE/nano- Al_2O_3 matrix in

the impregnation tank was determined to be 25°C , and long pot life of VE/nano- Al_2O_3 matrix can be confirmed at 25°C . The high reactivity of the VE/nano- Al_2O_3 matrix was observed from FTIR spectra and gel time at elevated temperature. From the morphological study of SEM photographs, excellent glass fiber impregnation by the VE/nano- Al_2O_3 matrix was observed. This demonstrates that the VE/nano- Al_2O_3 matrix was suitable for a pultrusion process.

The experimental results agree very well with the theoretical prediction and indicate that the kinetic autocatalytic model $d\alpha/dt = A \exp(-E/RT)\alpha^m(1-\alpha)^n$ is suitable for glass fiber-reinforced VE/nano- Al_2O_3 matrix composites. The average kinetic parameters can be calculated that include activation energy $E = 84.46$ kJ/mol, pre-exponential factor $A = 2.93 \times 10^5 \text{ min}^{-1}$, reactive orders $m = 0.632$, $n = 1.456$, and total reactive orders $m + n = 2.088$.

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