

Glass Fiber Reinforced Vinyl Ester Containing Nano- Al_2O_3 Composites for Pultrusion: Process Feasibility and Kinetic Analysis

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Introduction

Pultrusion is an efficient manufacturing processes for fabricating polymer composites parts of constant cross section [1]. 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 (PMCs) [2]. Fig.1 showed a schematic representation of the pultrusion process [3]. The nano- Al_2O_3 have unique properties which included high strength, high modulus, high conductivity, low thermal expanded coefficient, thermal impact resistance, high chemical stability, high electric insulation, and high acid, alkalinity, solvent resistance [4], it can increase the pultruded vinyl ester composites. Hence, this paper investigates a proprietary processes to manufacture glass fiber reinforced vinyl ester nanocomposites by pultrusion. To utilize vinyl ester prepolymer with nan- Al_2O_3 as matrices, glass fiber as reinforcements for pultrusion. By controlling the molecular weight, viscosity of matrices and through the self-designed pultrusion facility. The matrices were used directly and polymerized in the pultrusion die. It provides a new concept for *in-situ* pultrusion [5]. To study the process feasibility of resin as polymeric matrix to fabricate pultruded glass fiber composites, and to study the processing parameters by polymer kinetic analysis.

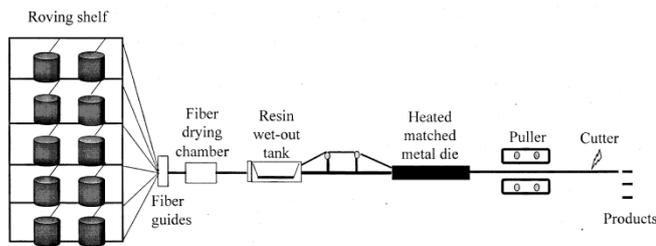


Fig.1 Flow chart of in-situ pultrusion machine.

Materials

The vinyl ester (VE) prepolymer used was bisphenol-A-type and was supplied by Swancor Co. Taiwan. It has a viscosity of 300 mPa.s at 25°C. The initiator (curing agent) used was t-butyl perbenzoate (TBPB), supplied from the Swancor Co. Taiwan; it has a specific gravity of 1.04. The continuous E-glass fiber roving was TGFR-P2200, which was obtained from the Taiwan Glass Industry Co., Taiwan, ROC; it has a filament diameter of 13.1 μm , a density of 2.54 g/cm^3 , a tensile strength of 3500 MPa, a elastic modulus of 73 GPa, and a elongation of 4.8% at 25°C. The nano- Al_2O_3 has a diameter of 38.2 nm, a specific surface area of 43.6 m^2/g , a specific gravity of 3.60.

Results and Discussion

Process feasibility study

Viscosity in the impregnation tank - As the suitable viscosity of prepolymer in the impregnation for pultrusion processes must be set at 500~2000 mPa.s. Table 1 shows the viscosity of VE with nano- Al_2O_3 at 25°C. When the nano- Al_2O_3 content was 6 phr, the viscosity of resin exceeded 2000 mPa.s, it was not suitable for pultrusion. When the nano- Al_2O_3 content exceeded 4 phr, the pultrusion process can not proceed, because the process was jammed in the die when the VE resin containing nano- Al_2O_3 exceeded 4 phr. Therefore, the suitable range for good fiber wetting out. The optimum nano- Al_2O_3 content in the impregnation tank was 1~3 phr.

Pot life - In order to provide a sufficient time for pultrusion processing, the pot life of resin (VE prepolymer containing nano- Al_2O_3) must be prolonged. Fig.2 shows the viscosity versus reaction time of resin at various temperatures. One can observe the viscosity of resin rises only 40 mPa.s (from 620 to 660 mPa.s) after 3 hr at 25°C. These results indicate that the pot life of resin are longer than 3 hr when the impregnation tank is set at 25°C, which provides a sufficient time for subsequent processing.

Reactivity - In the pultrusion process, the resin (VE prepolymer containing nano- Al_2O_3) and resin/glass fiber must have high reactivity, otherwise, they cannot be fabricated in a short time in the die. Fig. 3 shows the gel time of resin and resin/glass fiber (40/60 wt%) at various temperatures. From the figure, it is found that the resin have short gel time (< 60 sec) when the temperature is above 170°C. The gel time is very near between pure resin and resin/glass fiber due to the glass fiber do not react in the composites From these observations of Fig.3, the resin and resin/glass fiber have high reactivity at elevated temperature; thus the composites can be fabricated in a short time in the pultrusion die.

Morphology

In order to obtain the best properties of composites, the excellent fiber wet-out is very important. The morphology can be observed by SEM photographs. The fracture surfaces by SEM of pultruded unidirectional glass fiber reinforced resin (VE containing nano- Al_2O_3) composites are shown in Fig. 4. From the figure, it is can be seen that the glass fiber surface still retains a lot of resin after fracture tests. Therefore, excellent wet-out of glass fiber by FA resin can be observed.

Table 1. Viscosity of vinyl ester containing nano-Al₂O₃.

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

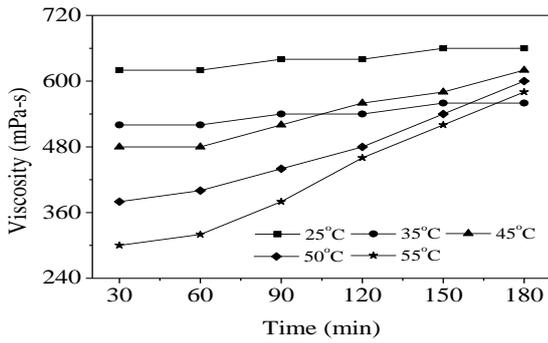


Fig.2 Viscosity of resin versus time at various temperature.

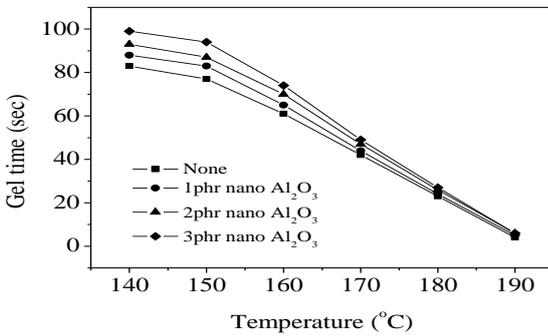


Fig.3 Effect of temperature on the gel time of the resin.

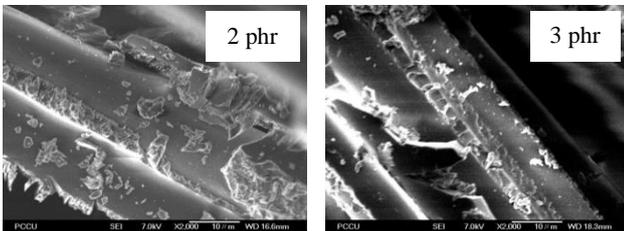


Fig.4 SEM of pultruded glass fiber reinforced resin (VE with nano-Al₂O₃) composites.

Kinetic analysis

The mechanistic kinetic model used in this study to describe the curing behavior of a resin (VE with 3 phr nano-Al₂O₃)/glass fiber (40/60 wt%) is based on an autocatalytic reaction. Details of the derivation are discussed elsewhere. The rate equation is given by equation (1)

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

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, n is the orders of reaction.

The heat evolved during the curing reaction and measured by the dynamic DSC thermogram at 10°C/min can be related to the conversion and conversion rate by

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

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

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

where α is the conversion at time t; Q_t is the reaction heat up to time t or temperature T; dH/dt is the rate of heat evolution per unit mass of resin at time t; $\beta = dT/dt$ is scan speed; 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 $\Delta H = 249.5 \text{ J/g}$ can be obtained. we can choose 100 data of $[\ln(d\alpha/dt), 1/RT, \ln \alpha, \ln(1-\alpha)]$ from the dynamic 10°C/min DSC runs, and then using a multiple regression technique computation to solve equation (5), one can obtain the kinetic parameters pre-exponential factor $A = 2.79 \times 10^5 \text{ min}^{-1}$, activation energy $E = 80.92 \text{ kJ/mol}$, and reaction orders $m = 0.634, n = 1.462$. Fig.5 illustrate conversion versus temperature of resin/glass fiber for the curing reaction at a scan speed of 10°C/min. The dashed lines represented the calculated values obtained from autocatalytic model of equation (1) with the aforementioned kinetic parameters, whereas the solid lines are obtained directly from the DSC thermogram experimental data by using equations (3) and (4). From Fig.5 results, one can observe that the experimental data agree very well with the theoretical prediction.

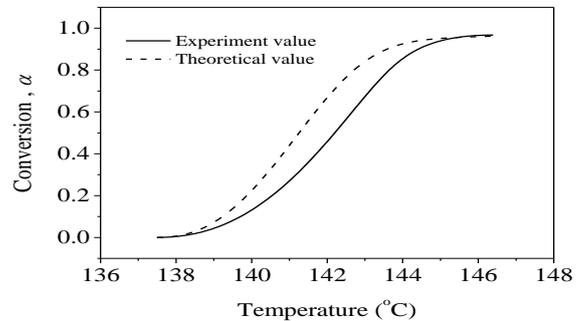


Fig.5 Experimental and theoretical value of α versus temperature by dynamic DSC at 10°C/min.

Acknowledgments

This research was funded by the National Science Council, Taiwan under the Contract No. NSC 99-2221-E-034-004.

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