The Unidirectional Glass Fiber Reinforced Furfuryl Alcohol for Pultrusion. II. Correlation of Processing Parameters for Optimizing the Process

Chin-Hsing Chen, I-Ken Chen

Department of Chemical and Materials Engineering, Chinese Culture University, Yang-Ming-Shan, Taipei, Taiwan

ABSTRACT: Unidirectional glass fiber reinforced furfuryl alcohol (FA) composites have been prepared by the pultrusion processes. The optimum processing parameters of the glass fiber reinforced FA composites by pultrusion has been studied. The effects of the optimum processing parameters on the properties (flexural strength, flexural modulus, notched Izod impact strength, glass transition temperature (T_g), dynamic shear storage modulus (E'), shrinkage ratio, and roughness) investigated including die temperature, pulling rate, postcure temperature and time, and filler type and content. Results show that the pultruded composites possessed various optimum pulling rates at different die temperatures. On the basis of the DSC diagram, the swelling ratio and the mechanical properties of pultruded composites, the optimum die temperature can be determined. The mechanical properties and T_g increase at a suitable postcure temperature and time. Furthermore, the properties which decrease due to the degradation of pultruded composites for a long postcure time will be discussed. The mechanical properties of pultruded composites reach a maximum value at various filler content corresponding to the talc and calcium carbonate, respectively, and then decreased. When the fillers are added to the pultruded glass fiber reinforced FA composites, the shrinkage ratio of composites become smaller, and the surface of composites became smooth. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1788–1796, 2011

Key words: pultrusion; glass fiber; furfuryl alcohol; processing parameters; composites

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] The annual growth rate of this process was about 17–20% over the past decade. In recent years, a number of resins have been used for the pultrusion process, including the thermoset resins (unsaturated polyester[5,6]; epoxy[7,8]; vinyl ester[9,10]; phenolic[11,12]; and furfuryl alcohol[13,14]) and thermoplastic resins (polybutylene terephthalate (PBT)[15]; polyamide 6 (Nylon 6)[16]; polypropylene (PP)[17]; polyphenylene sulfide (PPS)[18]; polyether ether ketone (PEEK)[19]; polystyrene (PS)[20,21]; acrylonitrile-butadiene-styrene copolymer (ABS)[22]; and polymethyl methylacrylate (PMMA)[23,24]). Figure 1 illustrates a schematic representation of the pultrusion process. During pultrusion, fibers are driven through a resin bath where good impregnation can be achieved using a resin of the correct viscosity (500–2000 mPa · s). After the resin excess is removed in preforming guides, the fiber/resin system acquires the desired shape and passes through the cure process in a heated die, which acts as a continuous reactor. Usually, various heating zones are provided along the die depending on the type of resin, the pulling speed, and the length of the die.[25]

To obtain the best mechanical properties and the optimum process condition for pultrusion, the processing parameters have to be investigated to optimize the pultrusion process. The parameters affecting the behavior of the composites during processing can be identified as die temperature, pulling rate, postcure temperature and time, and filler type and content. The objective of utilizing furfuryl alcohol (FA) for the pultrusion process is to take advantage of the unique properties of FA including excellent mechanical properties, outstanding chemical resistance, excellent flame resistance, low smoke emission, and high heat deflection temperature, etc.[26] FA have been used widely in reactor, piping, electroplate tank, and exhaust gas hood, etc.[27]

In this study, the pultrusion of glass fiber reinforced FA composites has been conducted using a proprietary process. A suitable viscosity range (500–2000 mPa · s) of FA prepolymer was synthesized from FA monomer and curing agent (*p*-toluene sulfonic acid) at a suitable
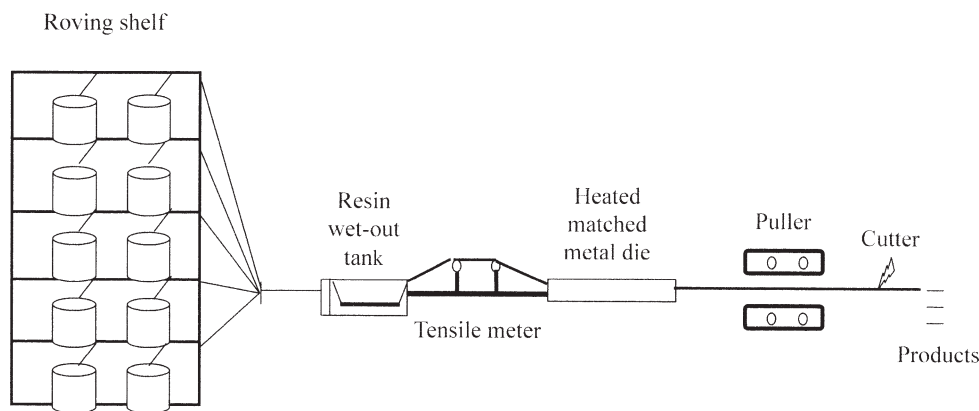
Figure 1 Flow chart of *in situ* pultrusion machine.

temperature. The prepolymers were used directly and polymerized in the die. This provides a new concept for *in situ* polymerization pultrusion. This article presents the processing parameters for optimizing the process of the unidirectional glass fiber reinforced FA composites by *in situ* polymerization pultrusion.

EXPERIMENTAL

Materials

The materials used in this study are listed in Table I. They include furfuryl alcohol (FA) monomer, catalyst (*p*-toluene sulfonic acid), FA prepolymer synthesized in this study, glass fiber, and two fillers.

Synthesis of furfuryl alcohol (FA) prepolymer

The furfuryl alcohol (FA) prepolymer was synthesized by heating FA monomer with 2.25 p.h.r. cat-

TABLE I
Materials Used in this Study

Material	Specification	Supplier
FA monomer	Furfuryl alcohol Specific gravity = 1.15 Viscosity = 15 mPa·s at 25°C	Chang Chun Plastics, Taiwan, ROC
Catalyst	p-toluene sulfonic acid Specific gravity = 1.2	Chang Chun Plastics, Taiwan, ROC
Glass fiber	Continuous E-glass fiber roving TGFR-P1200 Specific gravity = 2.54 Filament diameter = 17 μm Tensile strength = 3500 MPa Elastic modulus = 73 GPa Elongation = 4.8% at 25°C	Taiwan Glass Industry, Taiwan, ROC
Fillers	Talc Specific gravity = 2.71 Calcium carbonate Specific gravity = 2.7	Yin Chin, Taiwan, ROC Yin Chin, Taiwan, ROC

alyst (curing agent) of *p*-toluene sulfonic acid in a water bath and the temperature was maintained at 70°C. The reaction was permitted to exotherm upon stirring and under a nitrogen blanket until a suitable prepolymer viscosity was reached. To remove the reaction heat (exothermic), the synthesized prepolymer was quenched in an ice bath for 30 min, and then was stored at a low temperature below 5°C. The viscosity of synthesized FA prepolymer was measured by a Vibro viscometer. The polymerized temperature was set at 70°C. When the prepolymer viscosity reached 150 mPa·s, the synthesized prepolymer was quenched in an ice bath for 30 min. When the temperature returned to be at room temperature (25°C), the synthesized FA prepolymer viscosity was found to be a 700 mPa·s. The polymerized chemical reaction of furfuryl alcohol prepolymer was described by eq. (1), (see Part I).[28]

$$\tag{1}$$
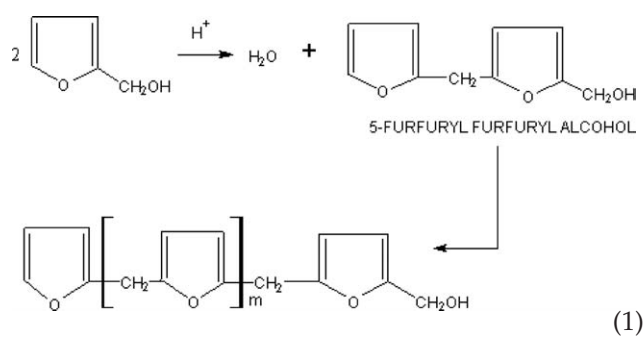
where H^+ is catalyst (*p*-toluene sulfonic acid).

Sample preparation

The 0–7 p.h.r fillers (talc, calcium carbonate) were added in FA prepolymer and was stirred continuously for 30 min to ensure mixing was complete. The FA prepolymers with glass fiber were used directly and *in situ* polymerized in the rectangular die. The pultrusion sample can be obtained at various pulling rates and die temperatures.
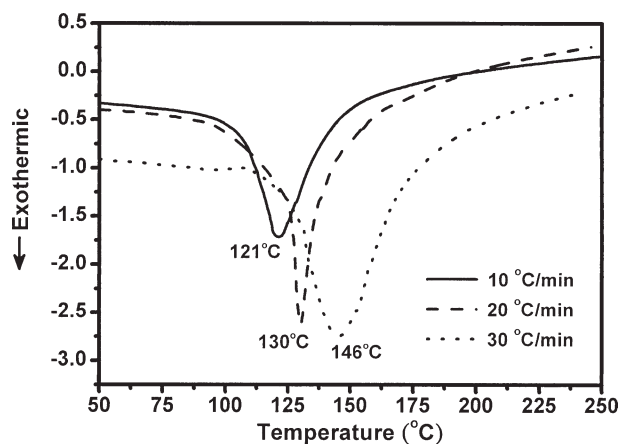
Figure 2 DSC thermograms of FA prepolymer by dynamic scanning.

Apparatus and measurement

The pultrusion machine was custom-designed. It consisted of multiple heating zones and a pultrusion die with dimensions of $820 \times 12.7 \times 3.19$ mm^3 and $820 \times 12.7 \times 2.10$ mm^3 (length $\times$ width $\times$ thickness), respectively. The surfaces of the stainless steel die were treated by chrome plating. The DSC (Differential Scanning Calorimetry) used was a Model 2010, DuPont, USA. The flexural properties were measured on an Instron 1123 universal testing machine (Instron, USA) following the specification of ASTM D-790. The sample dimensions were $127 \times 12.5 \times 3.0$ mm^3 (length $\times$ width $\times$ thickness), the span was 90 mm, and the crosshead speed was 2 mm min^{-1}. The sample dimensions were smaller than the dimensions of die, because of the sample shrinkage during processing. The notched Izod impact strength testing machine was a Gotech GT-7045 (Gotech, Taiwan) used in accordance with ASTM D-256. The sample dimensions were $63.5 \times 12.7 \times 3.0$ mm^3 (length $\times$ width $\times$ thickness), and the notch depth was 2.5 mm. The dynamic mechanical analyzer (DMA) was a DMA 2980 (DuPont, USA) from 0 to 300°C. The DMA system was of the resonance frequency type, and the sample dimensions were $50 \times 12.5 \times 2.0$ mm^3 (length $\times$ width $\times$ thickness). The heating rate was 5°C min^{-1}, and the frequency of oscillation was 1 Hz. The Poisson's ratio ν was 0.33. The measurement of swelling ratio q was determined using the following equation:

$$q = \frac{V}{V_0} = 1 + \frac{(W - W_0)D_0}{W_0 D_s} \qquad (2)$$

where V_0 = the volume of the unswollen pultruded composite, V = the volume of the swollen pultruded composite, W_0 = the weight of the unswollen pultruded composite, W = the weight of the swollen pultruded composite, D_0 = the den-

sity of pultruded composite, D_s = the density of solvent (chloroform).

The SEM photographs were obtained on a *S*-570 Hitachi scanning electron microscope (Hitachi, Japan). The microphotographs were taken on the surface obtained by fracturing the specimen in liquid nitrogen and then coating it with gold powder. The surface properties were obtained on a Metris-2001-NC atomic force microscope, AFM (Burleigh, USA).

RESULTS AND DISCUSSION

Effect of die temperature

Since the composite fabricated just in a short time in the pultrusion die, a proper higher die temperature will optimize the mechanical properties.

The operating process die temperature is determined by a differential scanning calorimetry (DSC). Five to ten milligrams of FA prepolymer sample is placed on the DSC cell. The test is conducted at scanning rates of 10, 20, and 30°C min^{-1}. The DSC result is shown in Figure 2 and Table II. It is shown that the exothermic peak reached maximum temperature at 121, 130, and 146°C, and the total heat generated (ΔH) during the polymerization are measured as 274.8, 260, and 244.1 J g^{-1} for 10, 20, and 30°C min^{-1} scanning, respectively. The conversion of reaction (extent of reaction) versus temperature for a series of dynamic DSC scanning at 10, 20, and 30°C min^{-1} is shown in Figure 3. The heat evolved during the curing reaction and measured by the dynamic DSC thermogram at 10, 20, and 30°C min^{-1} can be related to the conversion by

$$\Delta H = \int_0^t \frac{dQ_t}{dt} dt \qquad (3)$$

$$\alpha = \frac{Q_t}{\Delta H} \qquad (4)$$

where α is the conversion at time t; Q_t is the reaction heat up to time t or temperature T; and ΔH is the total heat of reaction for 100% conversion. From this figure, the final plateau value for the conversion decreases with increasing scanning rates. From Figure 3, a high conversion of reaction is measured when the reaction temperatures are set 205, 212, and

TABLE II
DSC Data of FA Prepolymer for Dynamic Scanning

Scan rate (°C min^{-1})	Peak start temp. (°C)	Peak onset temp. (°C)	Peak max. temp. (°C)	Peak end temp. (°C)	ΔH (J g^{-1})
10	75	103	121	205	274.8
20	92	122	130	212	260
30	105	130	146	224	244.1
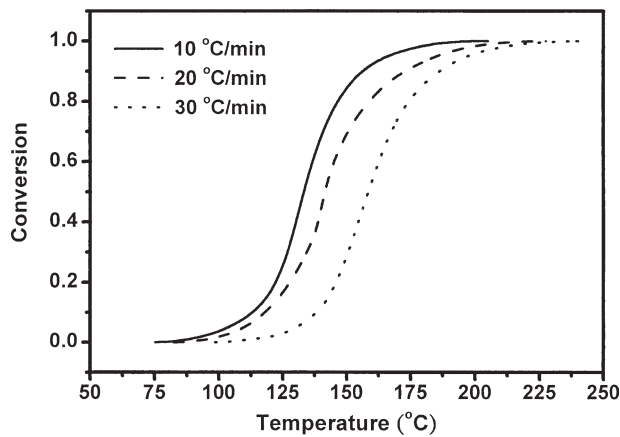
Figure 3 Conversion versus temperature of FA prepolymer for dynamic DSC.

Figure 5 Swelling ratio of pultruded glass fiber reinforced FA composites versus die temperature at various pulling rates.

224°C, respectively. From the above explanations, the die temperature should be higher than 205°C.

Figure 4 shows the mechanical properties (flexural strength) of pultruded glass fiber reinforced FA composites versus die temperature at various pulling rates. From this figure, one can observe that when the pulling rate is higher than 60 cm min^{-1}, the pultruded composites show that the higher the temperature, the better will be the mechanical properties obtained. This reasons is that the higher the die temperature, the higher the degree of polymerization (crosslinking) of composites. However, when the pulling rate is lower than 60 cm min^{-1}, the mechanical properties of the composites reached a maximum value at 230°C, and then decreases. This reasons that the higher the die temperature, the higher the degree of polymerization (crosslinking) of composites. Otherwise, when the die temperature is above 230°C, the composites began to degrade.

The degree of polymerization (crosslinking) and degradation of these composites can be explained
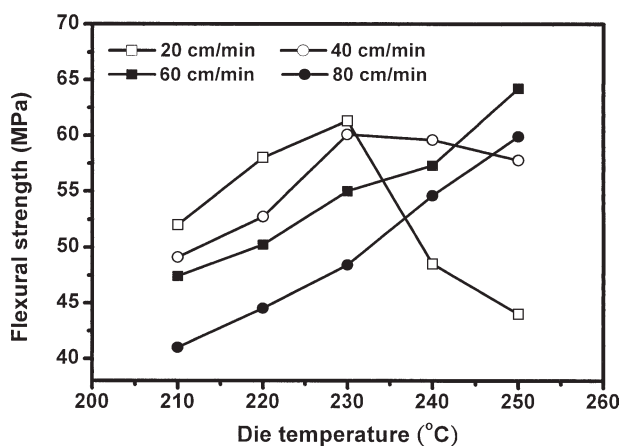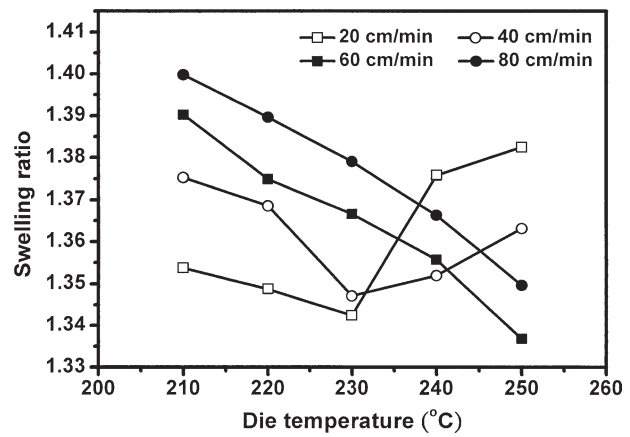
from their swelling ratios. The degree of polymerization of composites increases with decreasing of swelling ratio. The higher the degree of degradation, the greater is the swelling ratio of pultruded composites. Figure 5 shows the effect of die temperature on the swelling ratio of pultruded glass fiber reinforced FA composites. Comparing Figures 4 and 5, one can find that the higher the degree of polymerization (crosslinking), the smaller the swelling ratio of pultruded composites. Hence, when the swelling ratio is smaller, it can be derived the best mechanical properties of pultruded glass fiber reinforced FA composites. The die temperature cannot be higher than 230°C at low pulling rate. Otherwise, the composites may be degraded. The die temperature cannot be lower than 210°C, otherwise, the FA prepolymer are not polymerized completely.

From the DSC diagram, and the study of mechanical properties and swelling ratio, it may be
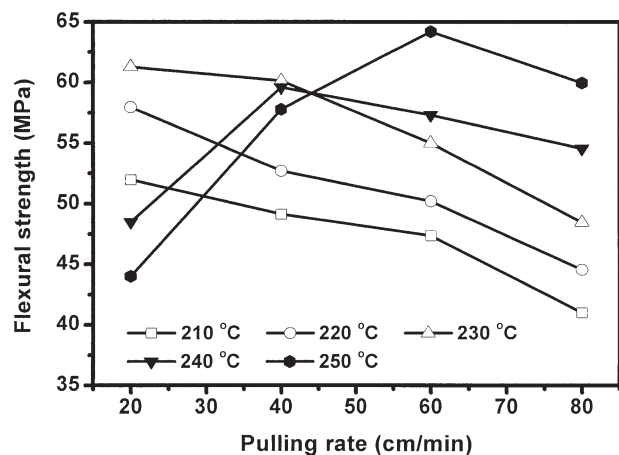

Figure 4 Flexural strength of pultruded glass fiber reinforced FA composites versus die temperature at various pulling rates.

Figure 6 Flexural strength of pultruded glass fiber reinforced FA composites versus pulling rate at various die temperatures.
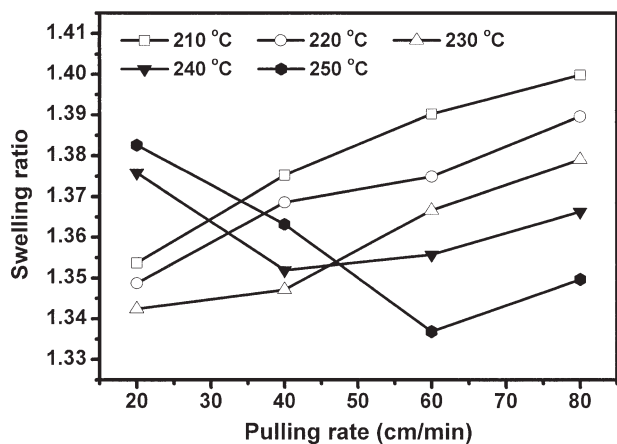
Figure 7 Swelling ratio of pultruded glass fiber reinforced FA composites versus pulling rate at various die temperatures.

concluded that the suitable die temperature is set at 230°C in this study.

Effect of pulling rate (in-line speed)

Since pultrusion is an automatic and continuous process for fabricating fiber reinforced plastics, the proper pulling rate is a critical parameter in the optimization of the production rate and the mechanical properties of the composites.

In general, the mechanical properties increase with decreasing of pulling rate if the composites do not degrade during pultrusion processing. For a lower pulling rate, the residence time of the resin in the pultrusion die will be longer; hence, the degree of polymerization will be higher and the wet-out of fibers will be better. Figure 6 shows the effect of pulling rate on the mechanical properties (flexural strength) of the pultruded glass fiber reinforced FA composites at various die temperature. From this fig-
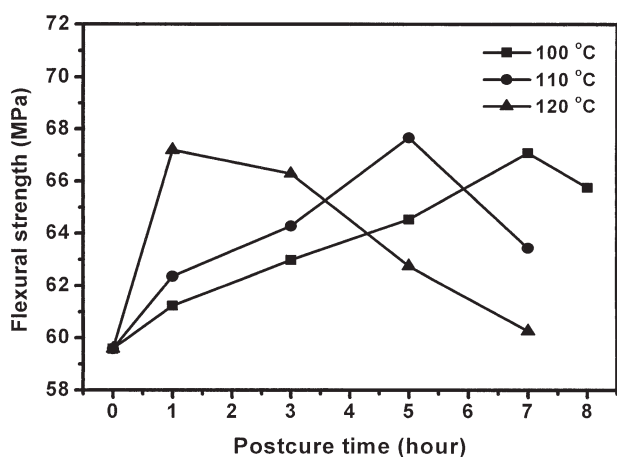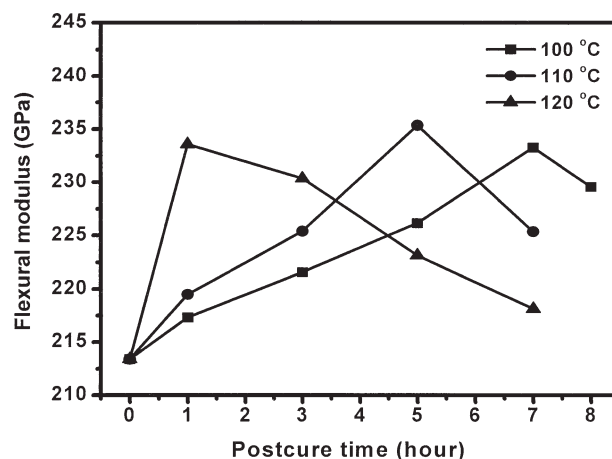

Figure 9 Flexural modulus of pultruded glass fiber reinforced FA composites versus postcure time at various postcure temperatures.

ure, one can observe that when the die temperatures are set between 210 and 230°C, the higher the pulling rate, the lower the mechanical properties of pultruded composites. This reasons that the lower the pulling rates, the higher the degree of polymerization (crosslinking) of composites. Furthermore, the mechanical properties of the composites reached a maximum value at 40 and 60 cm min^{-1} and then decrease, when the die temperatures are set at 240 and 250°C, respectively. This reason is that the lower the pulling rates, the higher the degree of polymerization (crosslinking) of composites. Otherwise, the pulling rates are set below 40 and 60 cm min^{-1} when the die temperatures are 240 and 250°C, respectively, the composites start to degrade due to the residence time of the resin in the pultrusion die will be longer at high temperatures. Figure 7 shows the effect of pulling rates on the swelling ratio of pultruded glass fiber reinforced FA composites. From this figure, one can observe that when the die
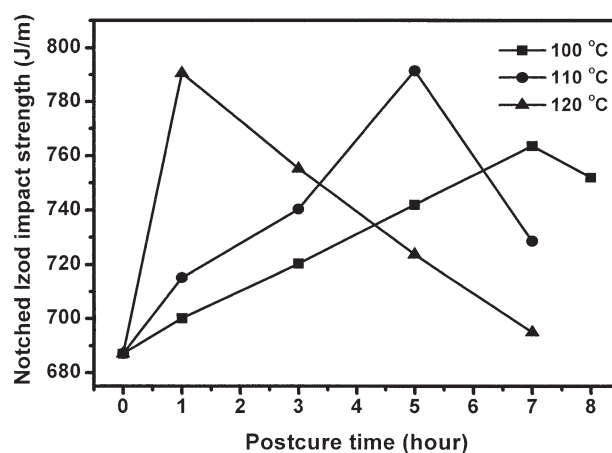

Figure 8 Flexural strength of pultruded glass fiber reinforced FA composites versus postcure time at various postcure temperatures.

Figure 10 Notched Izod impact strength of pultruded glass fiber reinforced FA composites versus postcure time at various postcure temperatures.

TABLE III
The T_g of Pultruded Glass Fiber Reinforced FA Composites Versus Postcure Time at Various Postcure Temperatures

Postcure temperature (°C)	Postcure time (hours)					
	0	1	3	5	7	8
	T_g (°C)					
100	176	179	183	187	192	190
110	176	181	187	195	185	–
120	176	194	190	181	177	–

temperature is lower than 230°C, the swelling ratio of pultruded composites increase with increasing of pulling rate. The reason is that when the pulling rate became higher, the degree of polymerization (cross-linking) became smaller. Hence, the swelling ratio of composites became greater. Furthermore, the swelling ratio of the composites reached a minimum value at 40 and 60 cm min^{-1} and then increase when the pulling rates are set at 240 and 250°C, respectively. This reason is that when pulling rates are set higher than 40 and 60 cm min^{-1} of die temperatures are 240 and 250°C, respectively, the lower the pulling rates, the higher the degree of polymerization (crosslinking) of composites, hence, the swelling ratio of pultruded composites increase with increasing of pulling rate. Otherwise, when pulling rates are set below 40 and 60 cm min^{-1} of die temperatures are 240 and 250°C, respectively, the swelling ratio of pultruded composites decrease with increasing of pulling rate. This reason is that the composites start to degrade due to the residence time of the resin in the pultrusion die will be longer at higher temperature. Comparing Figures 6 and 7, one can find that the mechanical properties of pultruded glass fiber reinforced FA composites increase with decreasing of swelling ratio.
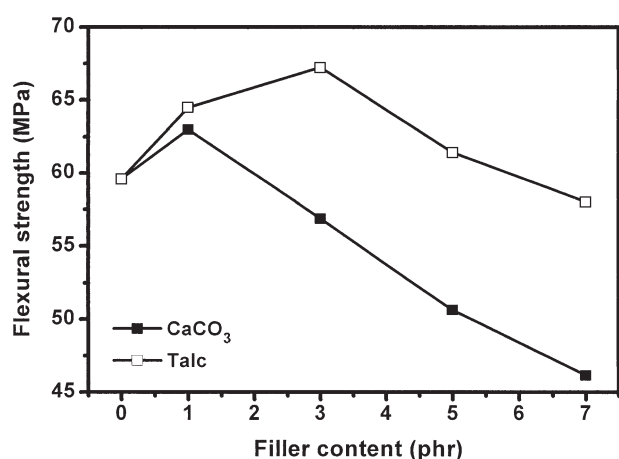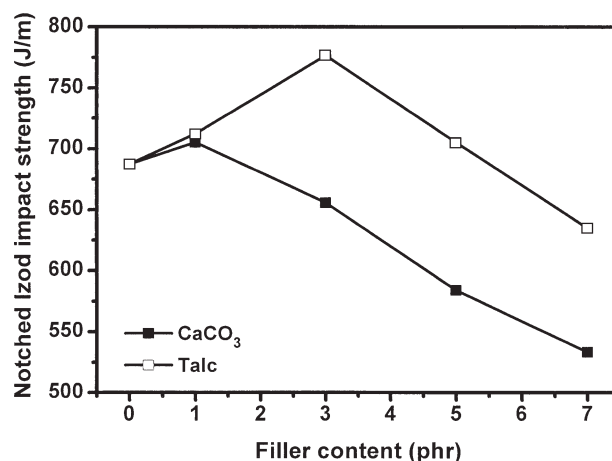

Figure 12 Notched Izod impact strength of pultruded glass fiber reinforced FA composites versus fillers content at various filler types.

From the above explanations, the optimum pulling rates are set at 20, 20, 20, 40, and 60 cm min^{-1} corresponding to die temperature of 210, 220, 230, 240, and 250°C, respectively.

Effect of postcure temperature and time

The main purposes of postcure process were to ensure complete reaction and to drive-off volatility from the composites. In the pultrusion process, the resin polymerizes in a short time in the die and the polymerization cannot be completed. Postcure process will encourage the unreacted prepolymer to react to a higher degree. Hence, postcure process will increase the degree of polymerization (crosslinking) of the polymer matrix and may improve the mechanical properties of pultruded composite materials.

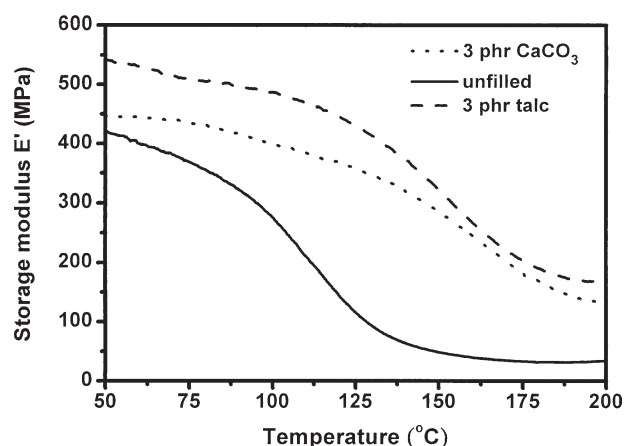Figures 8–10 illustrate the mechanical properties (flexural strength, flexural modulus, and notched

Figure 11 Flexural modulus of pultruded glass fiber reinforced FA composites versus fillers content at various filler types.

Figure 13 Dynamic shear storage modulus (E') versus temperature of pultruded glass fiber reinforced FA composites with 3 phr filler at various filler types.
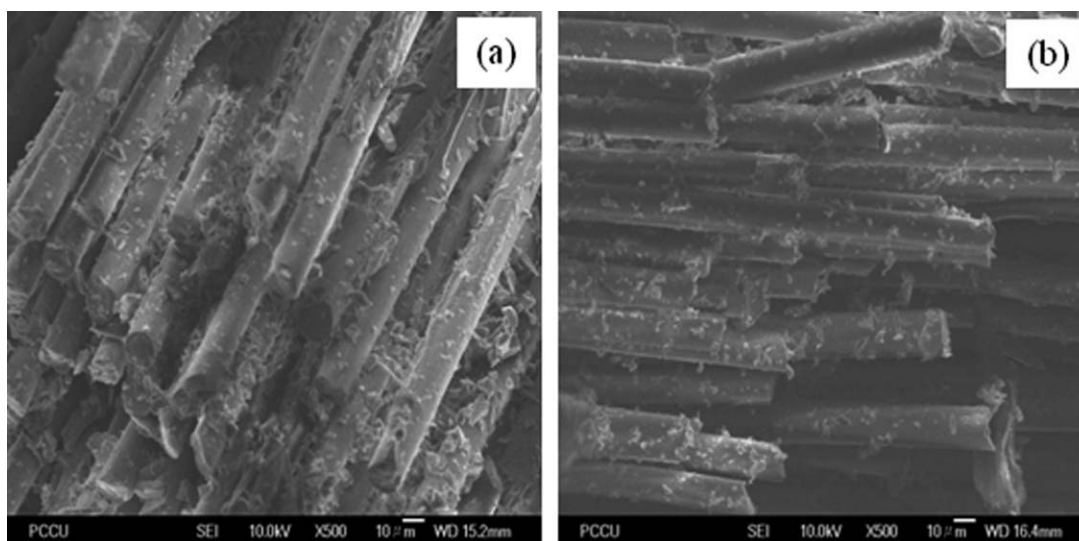
Figure 14 Fracture surfaces of SEM photographs of pultruded glass fiber reinforced FA composites with 3 phr fillers: (a) calcium carbonate and (b) talc.

Izod impact strength) of pultruded glass fiber reinforced FA composites versus postcure time at various postcure temperatures. From these results, it can be seen that the mechanical properties of pultruded composites reached a maximum value at postcure time of 7, 5, and 1 h corresponding to the postcure temperatures of 100, 110, and 120°C, respectively, and then decrease. Although the postcure process can improve the mechanical properties of pultruded composites, however, an excess of postcure process may result in the reduction of mechanical properties of pultruded composites. These reasons are that the postcure process can increase the degree of polymerization (crosslinking) of the polymer matrix. However, an excess of postcure process will create the degradation of polymer matrix. Table III showed the glass transition temperature (T_g) of pultruded glass fiber reinforced FA

composites versus postcure time at various postcure temperatures. This table shows that the T_g increased with increasing of postcure temperature and time, and the mechanical properties were raised. However, the T_g began to decrease when the pultruded composites were treated by postcure process after 7 h at 100°C, 5 h at 110°C, and 1 h at 120°C, and the mechanical properties were reduced. From the comparison between Table III and Figures 8–10, it can observe that the greater the mechanical properties, the higher the T_g of pultruded composites.

From the above explanation, the postcure process can improve the mechanical properties and T_g of pultruded composites. However, an excess of postcure process may be created the reduction of mechanical properties. The optimum postcure temperature and time were set at 120°C and 1 h.
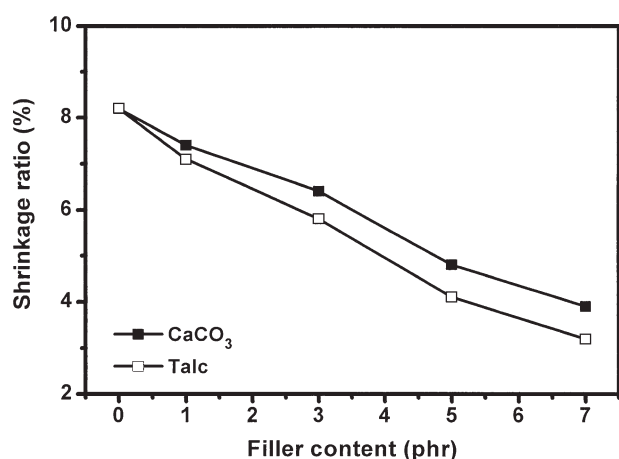

Figure 15 The change of shrinkage ratio of pultruded glass fiber reinforced FA composites versus filler content at various filler types.
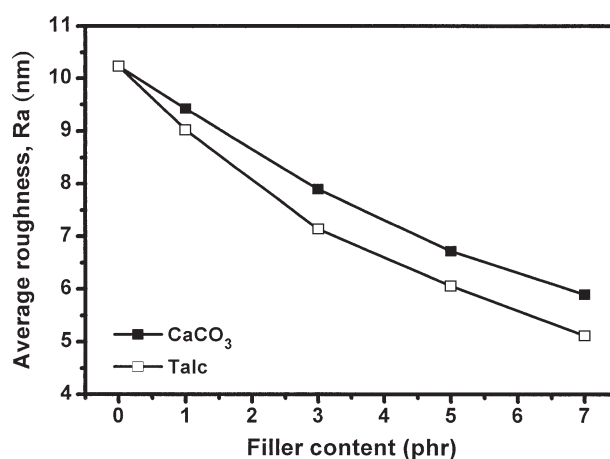

Figure 16 Average roughness (R_a) of pultruded glass fiber reinforced FA composites versus filler content at various filler types.
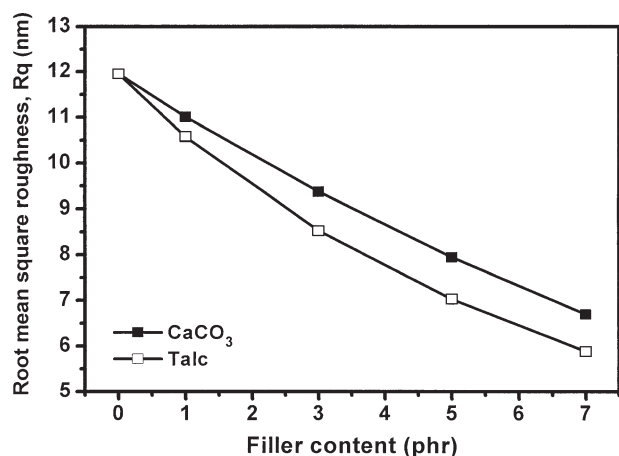
Figure 17 Root mean square roughness (R_q) of pultruded glass fiber reinforced FA composites versus filler content at various filler types.

Effect of filler types and contents

The purposes of adding fillers in the fiber reinforced pultruded composites are the following: (1) to improve the mechanical properties of the composite, (2) to reduce the shrinkage ratio of pultruded parts, and (3) to improve the surface of the composite. In a pultrusion process, if without filler, the mechanical properties of pultruded composites may be decreased, the shrinkage ratio may be increased, and the surfaces may become coarse. In this study, two fillers including talc and calcium carbonate ($CaCO_3$) are added to the pultruded glass fiber reinforced FA composites.

Figures 11 and 12 illustrate the mechanical properties (flexural strength and notched Izod impact strength) of pultruded glass fiber reinforced FA composites versus filler content at various filler types. From these figures, it can be seen that the mechanical properties of composites reach a maximum value at 1 and 3 phr filler content corresponding to the calcium carbonate and talc, respectively, and then decrease. The improvements of mechanical properties of composites with talc were superior to those with calcium carbonate. Figure 13 showed the dynamic shear storage modulus (E') versus temperature of pultruded glass fiber reinforced FA composites with 3 phr filler at various filler types. From this figure, one can observe that when the fillers are added to the composites, the E' of composites increase obviously. The improvements of E' of pultruded composites with talc were also superior to those with calcium carbonate. The morphology phenomena can be observed by SEM photographs. The fracture surfaces of pultruded glass fiber reinforced FA composites with 3 phr fillers were investigated by SEM as shown in Figure 14. From this figure, one can observe that these fillers are distributed evenly in the pultruded glass fiber reinforced FA compo-
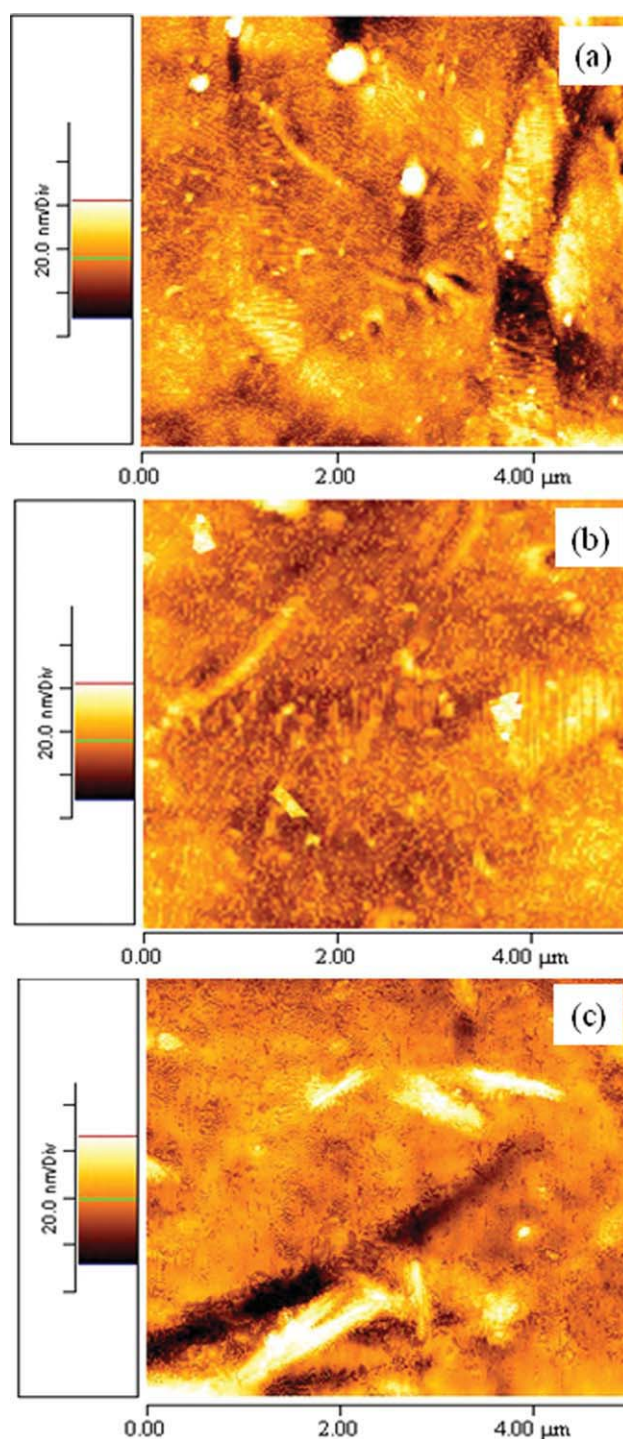

Figure 18 AFM micrographs of pultruded glass fiber reinforced FA composites: (a) without filler (b) with 3 phr $CaCO_3$ (c) with 3 phr talc. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sites which can improve the mechanical properties of pultruded composites. From above explanations, it is found that when the pultruded composites contained 3 phr talc, which will provide the best mechanical properties of pultruded composites.

One of purposes of adding fillers in the pultruded composites are reduced the composite shrinkage ratio.

The change of shrinkage ratio of pultruded glass fiber reinforced FA composites versus filler content at various filler types are shown in Figure 15. From this figure, one can observe that the shrinkage ratio of composites decrease with increasing of filler contents. In the meantime, the shrinkage ratio of composites containing talc was lower than those of containing calcium carbonate.

The surface properties of composites can be measured by atomic force microscope (AFM). From the AFM test, the smaller the values of average roughness (R_a) and root mean square roughness (R_q), the more smooth the surfaces of pultruded composites. The surface properties (R_a, R_q) of pultruded glass fiber reinforced FA composites versus filler content at various filler types is shown in Figures 16 and 17. From these figures, it can be seen that the R_a and R_q of pultruded composites decrease with increasing of filler contents, and the R_a and R_q of composites contain talc are lower than those containing calcium carbonate. Figure 18 showed the AFM micrographs of pultruded glass fiber reinforced FA composites with 3 phr fillers. From this figure, it can be seen that the surface of pultruded composites became more glossy when the composites contained fillers. From Figures 16–18, it can be concluded that when the fillers are added to the pultruded glass fiber reinforced FA composites. The surface of composites will become smooth.

CONCLUSIONS

A proprietary pultrusion process has been successfully applied to prepare unidirectional glass fiber reinforced FA composites. The effect of processing variables on the properties of glass fiber reinforced FA composites by pultrusion has been studied.

From the DSC diagrams, swelling ratio and mechanical property tests, The die temperature cannot be higher than 230°C at low pulling rate, otherwise the composites may be degraded. The die temperature cannot be lower than 210°C, otherwise, the FA prepolymer are not polymerized completely. It may be concluded that the suitable die temperature is set at 230°C in this study. The optimum pulling rates are set at 20, 20, 20, 40, and 60 cm min^{-1} corresponding to die temperature of 210, 220, 230, 240, and 250°C, respectively. The mechanical properties increase at a suitable postcure temperature and time, and decrease due to the degradation of composite materials for a long postcure time. The optimum postcure temperature and time were set at 120°C and 1 h. The mechanical properties of pultruded composites reach a maximum value at 1 and 3 phr filler content cor-

responding to the calcium carbonate and talc, respectively, and then decrease. The improvements of mechanical properties of composites contain talc are superior to those containing calcium carbonate. The shrinkage ratio of composites decrease with increasing of filler contents, and the shrinkage ratio of composites contain talc are lower than those containing calcium carbonate. It can be seen that the R_a and R_q of pultruded composites decrease with increasing of filler contents, and the R_a and R_q of composites contain talc are lower than those containing calcium carbonate. This means that when the fillers are added to the pultruded composites, the surface of composites will become smooth.

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