Pultruded Fiber-Reinforced Poly(methyl Methacrylate) Composites. I. Effect of Processing Parameters on Mechanical Properties

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SYNOPSIS

A feasibility study of pultrusion of fiber-reinforced thermoplastic PMMA composite has been conducted using a proprietary method. Effect of processing parameters, preparation of methyl methacrylate (MMA) prepolymer on the mechanical properties (tensile, flexural strength and modulus, impact strength, etc.) of fiber-reinforced PMMA composites by pultrusion has been studied. Processing parameters investigated included pulling rate, die temperature, postcure time and temperature, and filler content. From the study of Brookfield viscometer and FTIR spectrum the processing conditions can be defined. It was found from SEM photographs that the wetting out of fibers by PMMA resin was complete, and the fiber bundles were distributed evenly in the PMMA matrix. From the study of ^{1}H-NMR, GPC, and Brookfield viscometer, the conversion, molecular weight, and viscosity of MMA prepolymer data were obtained. From the DSC diagram, molecular weight measurement, and the rule of polymerization rate, the optimum die temperature was determined. It was found that the mechanical properties increase with increasing filler content and postcure temperature, and with decreasing die temperature and pulling rate.

INTRODUCTION

Pultrusion is an automatic and continuous process for fabricating fiber-reinforced plastics. Recently, great attention has been paid to it, and it has emerged as one of the most versatile and cost-effective processes of the composite industry. In the past, developments were of innovative modifications of the basic process[1-4] and new matrices. The application of pultrusion to manufacture continuous profiles of composite materials is expanding rapidly.[5] These materials are receiving widespread applications in sporting goods, corrosion resistant parts, architecture, transportation, agriculture, chemical engineering, electronic and electrical engineering, aircraft and aerospace, etc.[6-9]

The pultrusion process is an integral system that involves the pulling machine, resin preparation, type of reinforcement, processing parameters, etc. Most of the literature published[10-16] illustrates applications and some aspects of pultruded products instead of studying the resin formulations, processing variables, and relations between them, or only describes them for thermoset resins.[17-24] Recently, the resin formulations and processing parameters for thermoplastic matrix pultruded composites have been studied.[25-27] However, the major limitation to widespread use of thermoplastic resin for pultrusion is their poor fiber wet-out due to high melt viscosity (500,000–1,000,000 cps for thermoplastics versus 100–5000 cps for thermoset). This study investigated a novel technique for making continuously reinforced thermoplastic PMMA composites. The decision was made to examine the effects of these variables on the physical properties. This information would also be pertinent in order to enhance the development of the pultruded thermoplastic matrix process.

In this study, the methyl methacrylate (MMA) prepolymer with a suitable viscosity (500–2000 cps) was first synthesized from its monomer, and then was used directly and polymerized in the die. It provides a new concept for *in situ* thermoplastic pul-
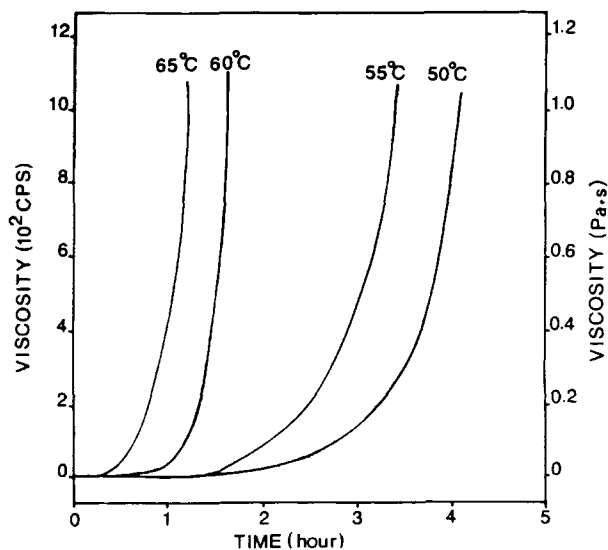

Figure 1   Viscosity of synthesized MMA prepolymer at various temperatures.

trusion.[28,29] The objective of this paper is to study the preparation method of MMA prepolymer and to investigate the effect of processing parameters (pulling rate, die temperature, postcure, and filler level) on the composite properties.

EXPERIMENTAL

Materials

The methyl methacrylate (MMA) monomer used in this research was a purified industry grade and was supplied by the Kaohsiung Monomer Co., Taiwan, Republic of China. The MMA prepolymer was synthesized in this study. The initiator benzoyl peroxide (BPO) used was a guaranteed reagent, which was obtained from the Kanto Chemical Co., Japan. The continuous E-glass fiber roving reinforcement used in this research was 764-NT-218 and supplied

by the PPG Co. (U.S.A.), which had a filament diameter of 13.1 μm, a tensile strength of 206 ksi, and a density of 2.54 g cm^{-3}. Three fillers were used in the present study, namely, calcium carbonate (Yin Chin Co., Taiwan, R.O.C.), which had a density of 2.7 g cm^{-3}, pyrogenic silica (Haur Hua Co., Taiwan, R.O.C.), which had a density of 2.1 g cm^{-3}, and talc (Cheng Shin Co., Taiwan, R.O.C.), which had a density of 2.71 g cm^{-3}.

Preparation of MMA Prepolymer

In this study, the methyl methacrylate prepolymer was synthesized by heating the inhibitor-free monomer in a water bath at 55°C. The reaction was permitted to exotherm upon stirring and under a nitrogen blanket until a suitable prepolymer viscosity was reached. In order to remove the reaction heat, the synthesized prepolymer was immersed in an ice bath for 30 min, and then was stored at a low temperature below about 20°C.

The viscosity of synthesized MMA prepolymer was measured by a Brookfield viscometer as shown in Figure 1. The optimum synthesis temperature was found to be 55°C. When the temperature is lower than 55°C, the processing time will be too long to process; however, when the temperature is higher than 55°C, the viscosity of MMA prepolymer cannot be controlled easily.

Apparatus

The pultrusion machine used was custom designed and consisted of a pultrusion die and multiple heating zones with dimensions of 0.319 × 1.27 × 82.0 cm (thickness × width × length), as shown in Figure 2. The surfaces of the stainless steel die have been treated by chrome plating. Viscosities were measured with a Brookfield RVF model viscometer during the synthesis of MMA prepolymer. The GPC (Gel Permeation Chromatography) utilized was a Unical 3-02 (Viscotek Co., U.S.A.). The DSC (differential
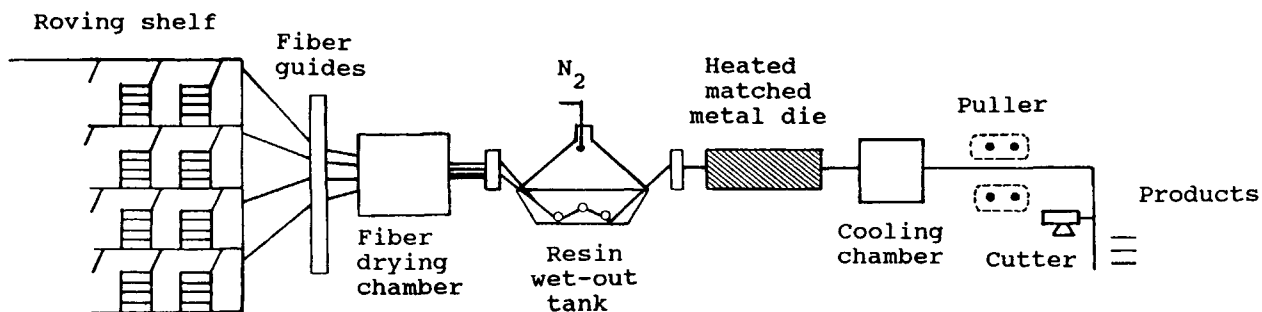

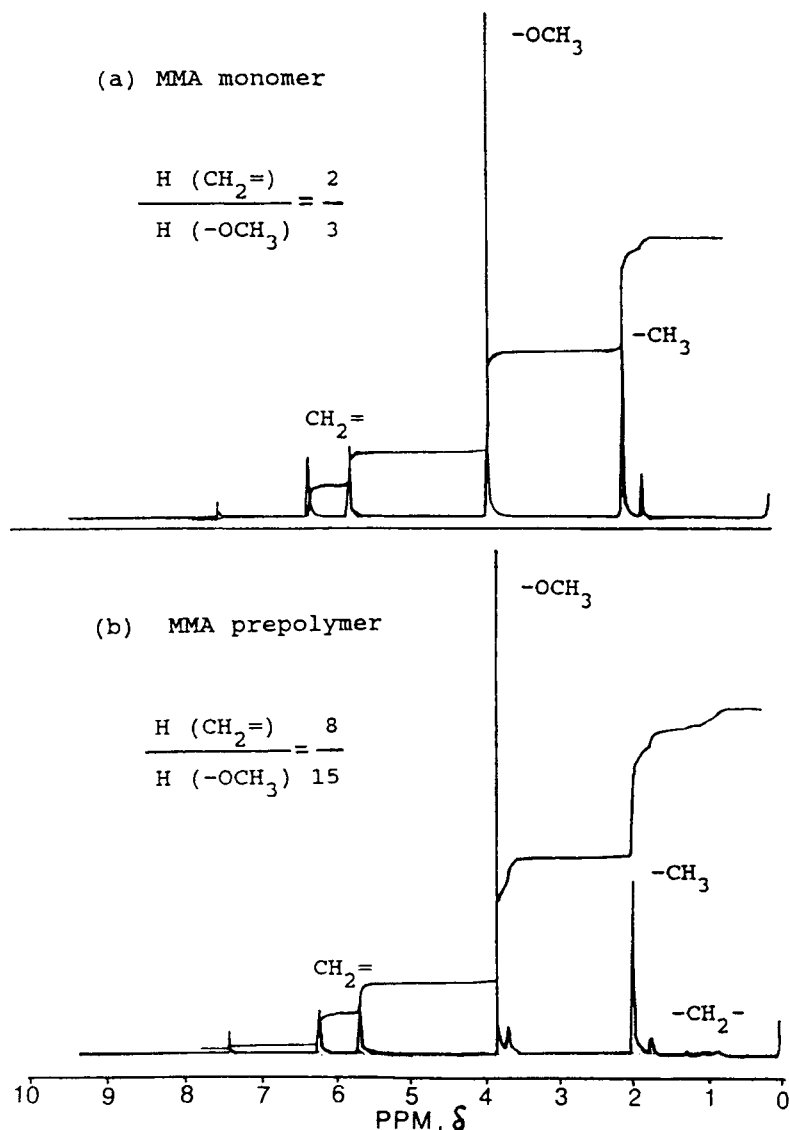**Figure 2**   Flow chart of pultrusion machine.

Figure 3   The ^{1}H-NMR spectrum of (a) MMA monomer and (b) MMA prepolymer.

scanning calorimetry) used was a Model 910 (Du Pont Co., U.S.A.). A universal material testing machine was used for the mechanical property tests, namely an Instron 1123 (Instron Co., U.S.A.). The impact strength testing machine utilized was a TMI-43-1 (Testing Machine Inc., U.S.A.). The SEM (Scanning Electron Microscope) used was a S-570 (Hitachi Co., Japan).

RESULTS AND DISCUSSION

Properties of MMA Prepolymer

Figure 3 shows the ^{1}H-NMR spectrum of (a) MMA monomer and (b) MMA prepolymer. The functional group —OCH$_3$ in MMA monomer was unchanged in the reaction; however, the functional group CH$_2$= in monomer was converted partially to —CH$_2$— after polymerization. The number of hydrogen atoms in —OCH$_3$ of MMA monomer remained constant; however, the number of hydrogen atoms in CH$_2$= decreased after polymerization. From the integral curves of Figure 3(a), the ratio of hydrogen atoms in CH$_2$=/—OCH$_3$ is equal to 2/3 before polymerization, and from Figure 3(b) the ratio equals about 8/15 after polymerization. From the equation 2/3(1 − x) = 8/15, the ratio of conversion (x) was calculated as 0.2. Table I summarizes the physical properties of methyl methacrylate monomer and its prepolymer.

Table I   Physical Properties of Methyl Methacrylate (MMA) Monomer and Its Prepolymer

Properties	Unit	MMA Monomer	MMA Prepolymer
Molecular weight	—	100	1200–1500
Specific gravity	—	0.94	1.04
Conversion	%	—	20
Viscosity (25°C)	cps	10	900–1200
Solubility in water (30°C)	wt %	1.5	1.1

Process Feasibility Study

Generally, the thermoplastic resin used for *in situ* pultrusion process must possess the following characteristics: (1) high reactivity, (2) long pot life in the impregnation tank, and (3) good wetting ability between fiber and resin. Generally, when the methyl methacrylate was polymerized,[30] one can observe from the Fourier transform infrared (FTIR) spectrum that the absorption peaks disappear at 1630 cm^{-1} (C=C), 1300 and 1330 cm^{-1} (CH$_2$); the CH$_2$ group in the polymer chain appears simultaneously at 750 cm^{-1}. Figure 4 shows that the FTIR spectrum of MMA prepolymer which polymerized at 160°C for 60 s in this study. It was found that the C=C peak at 1630 cm^{-1} and CH$_2$ at 1300 and 1330 cm^{-1} disappear and the CH$_2$ peak at 750 cm^{-1} appears clearly. From the observation of these peaks, the PMMA resin can be polymerized in a short time;[31,32] thus the composites can be fabricated in a short time in the die. In this study, the MMA prepolymer was synthesized in this laboratory, to a weight average molecular weight of around 1200–1500, and a viscosity of about 900–1200 cps (at 25°C). As shown in Figure 5, one can observe that the MMA prepolymer shows long pot life, and the viscosity of the prepolymer rises only 200 cps after 9 h at 30°C and 500 cps after 8 h at 35°C, which gives sufficient time for subsequent processing.

The longitudinal, cross-section, and fracture surfaces of pultruded glass-fiber-reinforced PMMA composites were investigated by scanning electron microscope as shown in Figure 6. From Figures 6(a) and (b), one can observe that the fiber bundles are distributed evenly in the PMMA matrix. Figure 6(c) shows that the wet-out of fibers by PMMA resin is complete.
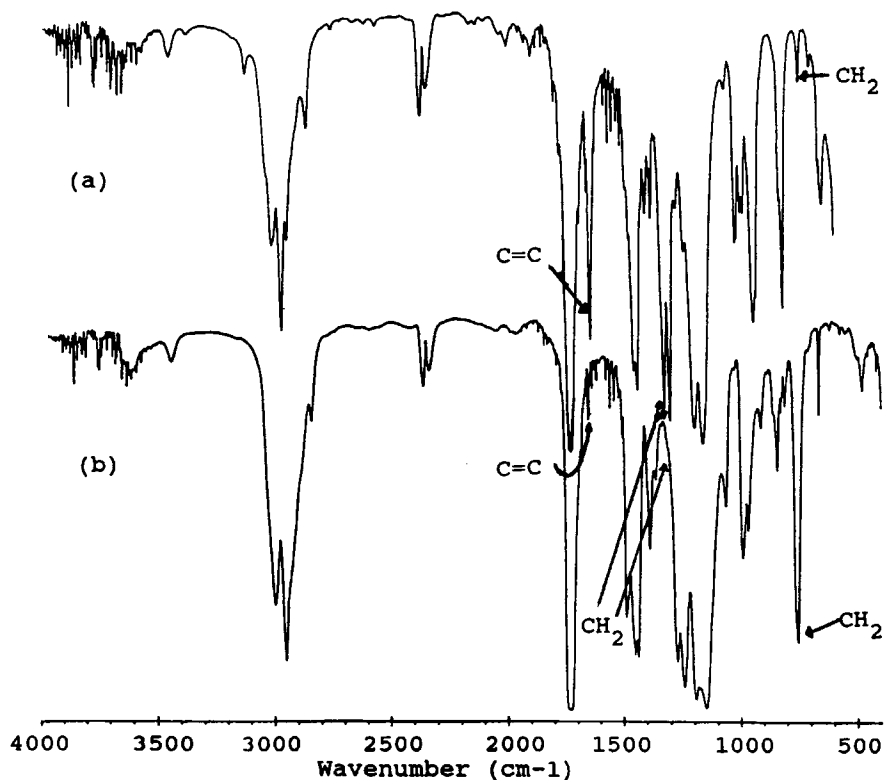

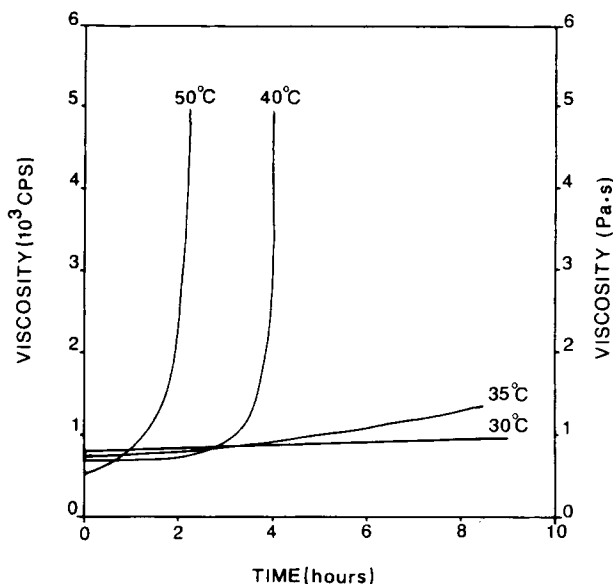**Figure 4**   The FTIR spectrum of (a) MMA prepolymer and (b) PMMA.

Figure 5 Viscosity of MMA prepolymer vs. time at various temperatures.

Pulling Rate (In-Line Speed) Effect

Since pultrusion is an automatic and continuous process for fabricating fiber reinforced plastics, a proper pulling rate will optimize production rate and the mechanical properties.

Figure 7 shows the effect of pulling rate on the tensile, flexural, and impact strength of pultruded glass-fiber-reinforced PMMA composites. In general, the mechanical properties increase with decreasing pulling rate. For a lower pulling rate, the residence time of resin in the die will be longer;

hence the degree of polymerization will be higher, and the wet-out of fiber will be better. Figure 8 shows the IR spectrum of pultruded glass-fiber-reinforced PMMA composites at various pulling rates, it was found that the C=C peaks at 1630 cm^{-1} decreased with decreasing pulling rate. From the GPC study as shown in Table II, when the die temperature was 140°C, the lower the pulling rate, the higher the number and weight average molecular weights. When the pulling rate is lower than 40 cm/min, the production rate will be too low to be utilized in an industrial application. However, when the pulling rate is higher than 100 cm/min, the mechanical properties will be reduced due to low molecular weight of PMMA and poor fiber impregnation. An optimum pulling rate at 40–100 cm/min was found in this study.

As shown in Figures 9(a)–9(d), the SEM photographs show the fracture surface of pultruded glass-fiber-reinforced PMMA composites at various pulling rates. From SEM photographs one can observe the impregnation of glass fiber in PMMA matrix. The lower the pulling rate, the better the fiber wet-out.

Die Temperature Effect

The operating process die temperature was determined by differential scanning calorimetry (DSC). Five to 10 milligrams of MMA prepolymer sample was placed in the DSC cell. Isothermal scanning at 120, 130, 140, and 150°C was conducted. The result of the isothermal scanning test is shown in Figure 10. These DSC curves summarize the comparison
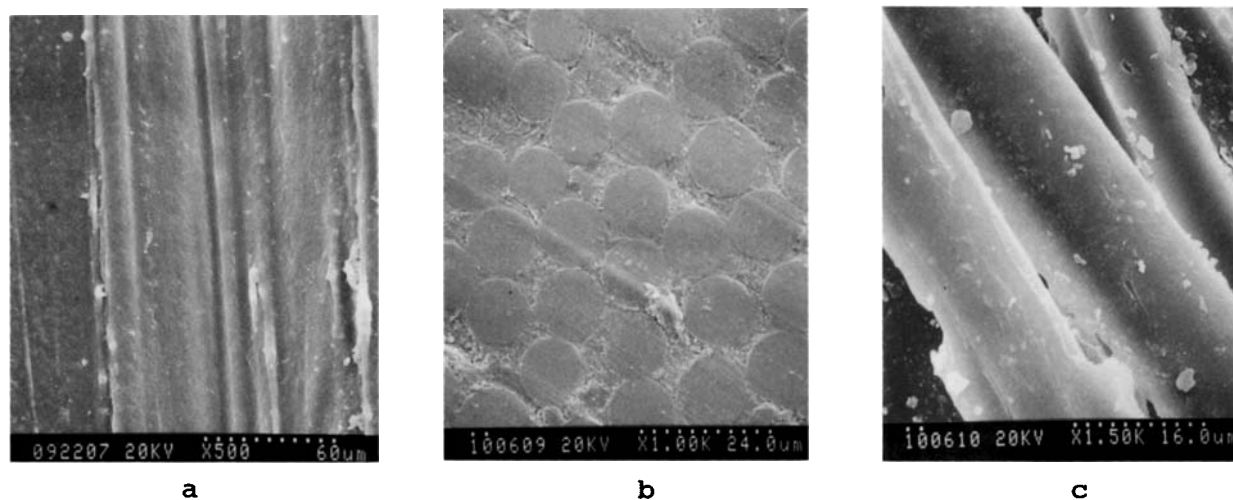

Figure 6 Scanning electron micrograph (SEM) of pultruded glass-fiber-reinforced PMMA composites: (a) longitudinal; (b) cross section; (c) fracture surface.
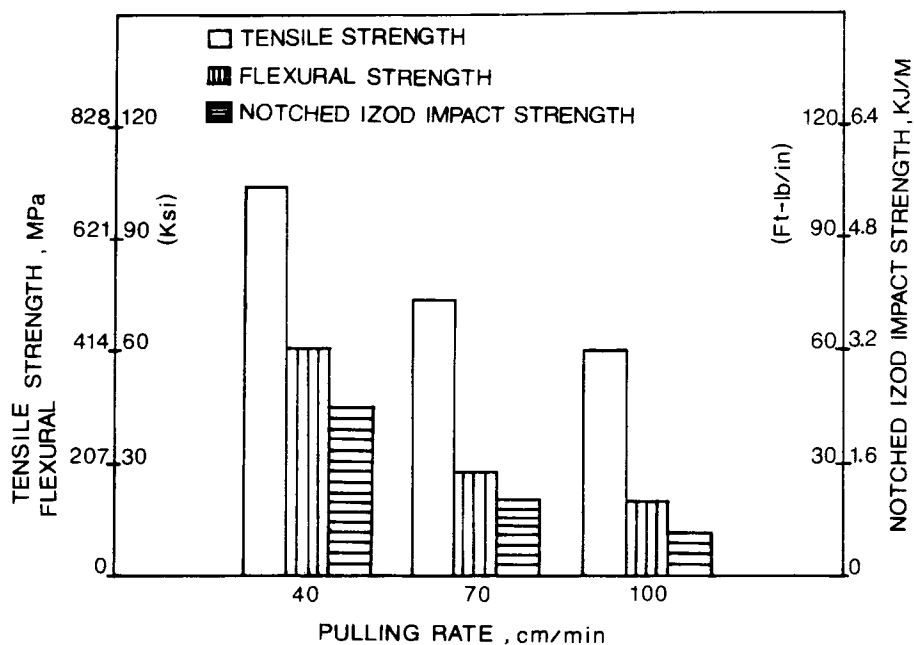
Figure 7 Tensile strength, flexural strength, and notched Izod impact strength of pultruded glass fiber reinforced PMMA composites vs. pulling rate.

of four processing temperatures, from which the polymerization rate (time) can be obtained. When the temperatures were set at 120, 130, 140, and 150°C, the exothermic peaks reached their maximum at 2.7, 2.2, 1.5, and 0.5 min, respectively. These results indicate that the higher the temperature, the faster the polymerization rate.

From the rule of polymerization rate as proposed by Odian,[33]

$$\ln X_n = \ln(A_p/A_d \times A_t)^{1/2}$$
$$+ \ln([M]/(f \times [I])^{1/2}) - E_{X_n}/RT \quad (1)$$

where A_p = the collision frequency factor of propagation step (L/mol s), A_d = the collision frequency factor of initiator decomposition (L/mol s), A_t = the collision frequency factor of termination step (L/mol s), [M] = monomer concentration (mol/L), [I] = initiator concentration (mol/L), f = initiator efficiency, R = gas law constant, T = Kelvin temperature, E_p = the activation energy of propagation, E_d = the activation energy of initiator decomposition, and E_t = the activation energy of termination. Since A_p, A_d, A_t, f, [I], and [M] are all positive,

$$\ln X_n = K - E_{X_n}/RT \quad (2)$$

Since K is a positive constant, E_{X_n} can be expressed as

$$E_{X_n} = E_p - (E_d/2) - (E_t/2) \quad (3)$$

which is the overall activation energy at the degree of polymerization, X_n.

Since E_p = 26.4 kJ/mol, E_d = 124.3 kJ/mol, and E_t = 11.9 KJ/mol,[34] E_{X_n} was calculated as −41.7 kJ/mol; X_n (degree of polymerization) decreases rapidly with increasing temperature. The molecular weight of PMMA was obtained at the pulling rate of 40 cm/min by GPC tests as shown in Table III. From this figure, it can be seen that the number and weight average molecular weight increase with decreasing die temperature. Hence, the die temperature cannot be lower than 140°C; otherwise the composites cannot be processed in a short time in the die. The die temperature should not be higher than 180°C, or the molecular weight will decrease sharply. Hence, from the DSC diagram, molecular weight measurement, and the rule of polymerization rate, one can observe that the suitable die temperature range in this study is between 140 and 180°C.

As shown in Figures 11 and 12, the lower the die temperature, the better the mechanical properties will be obtained. When the pulling rate of glass-fiber-reinforced PMMA composites are less than 60
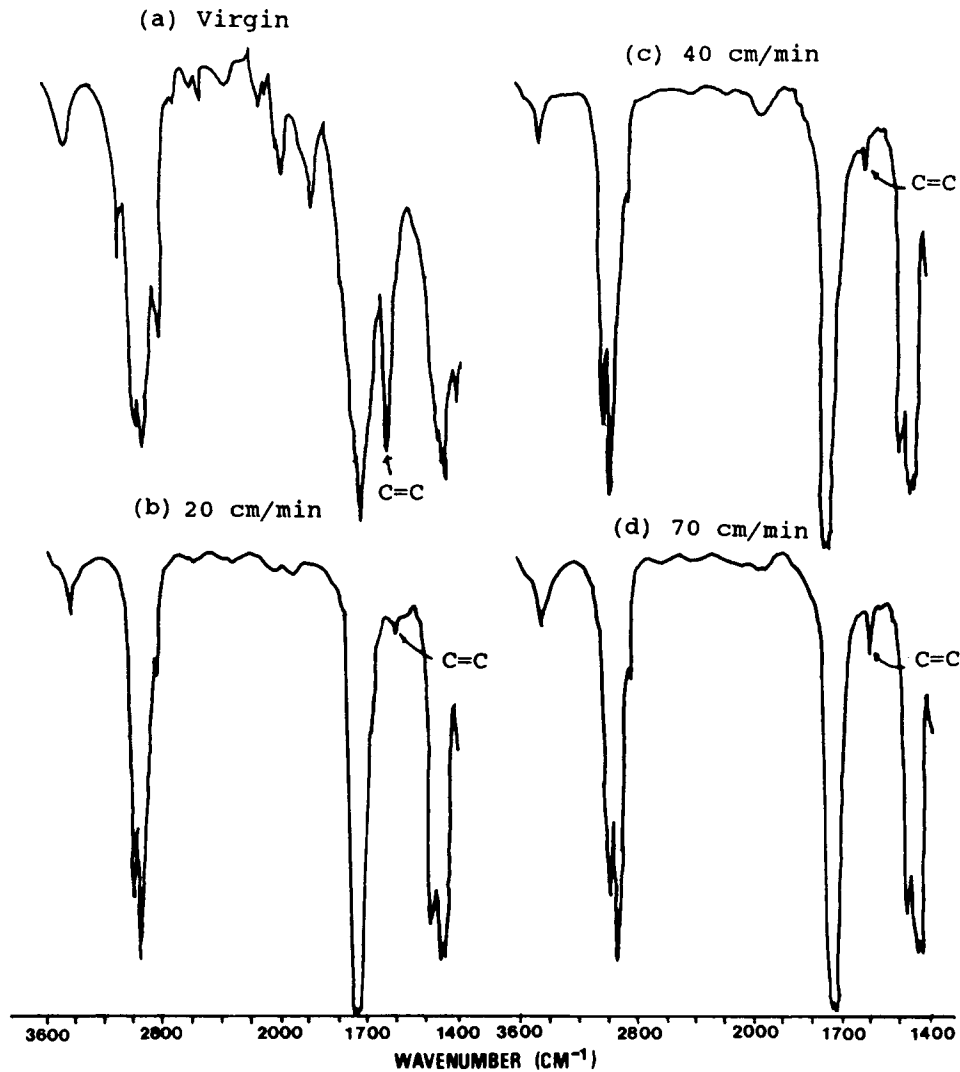
Figure 8   IR spectrum of pultruded glass-fiber-reinforced PMMA composites at various pulling rates (cm/min): (a) virgin (prepolymer); (b) 20; (c) 40; (d) 70.

cm/min, the mechanical properties increase with decreasing die temperature. When the pulling rate is above 60 cm/min and at a die temperature of 140°C, the monomers do not polymerize completely; hence the mechanical properties decrease sharply.

Filler Level Effect

The major purposes of adding fillers in the fiber-reinforced pultruded composites are the following: (1) to reduce the shrinkage of pultruded parts, (2) to improve the properties and surface of the product, and (3) to reduce the cost of production. In the pultrusion process, if there is a lack of filler, the surfaces of pultruded product would become coarse and the mechanical properties may be decreased.

In this study, three fillers including calcium carbonate, pyrogenic silica, and talc were used. Figures 13 and 14 show tensile strength and flexural strength

Table II   Weight and Number Average Molecular Weights (M_w, M_n), and Polydispersity Indices (PDI) of Pultruded Glass Fiber-Reinforced PMMA Composites versus Pulling Rate

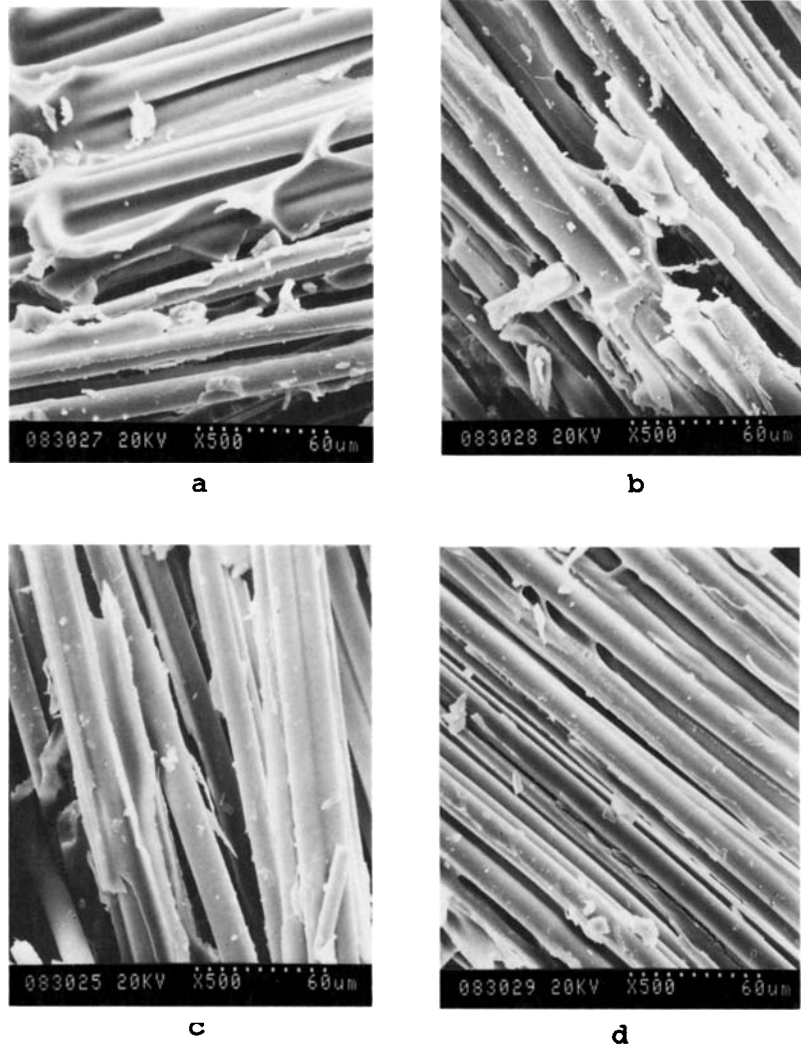| Pulling Rate (cm/min)	M_w (10^4)	M_n (10^4)	PDI (M_w/M_n)
20	26.2	6.65	3.94
40	23.4	5.49	4.26
70	14.5	2.38	6.09
100	10.7	1.71	6.26

Figure 9 The SEM photographs of fracture surface of pultruded glass-fiber-reinforced PMMA composites at various pulling rates (cm/min): (a) 40; (b) 70; (c) 100; (d) 130.
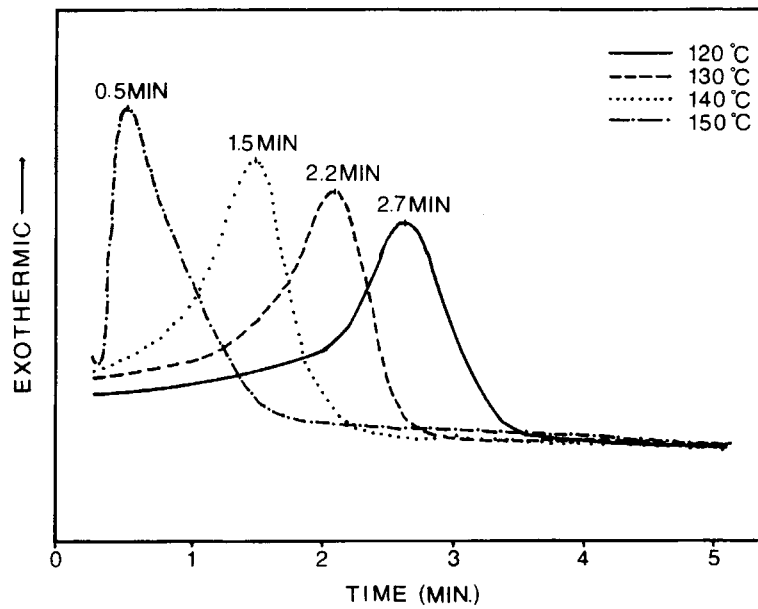

Figure 10 DSC thermograms of MMA prepolymer by isothermal scanning at: (———) 120°C; (— — —) 130°C; (· · ·) 140°C; (— · — ·) 150°C.

Table III Weight and Number Average Molecular Weights (M_w, M_n) and Polydispersity Indices (PDI) of Pultruded Glass Fiber Reinforced PMMA Composites versus Die Temperature

Die Temperature (°C)	M_w (10^4)	M_n (10^4)	PDI (M_w/M_n)
140	23.4	5.49	4.26
160	17.1	3.12	5.48
180	11.9	1.78	6.67
200	7.7	1.10	7.00

of pultruded glass-fiber-reinforced PMMA with varying filler content. It is shown that the tensile and flexural strength of composites increase gradually from 0 to 5 phr of calcium carbonate and talc, and then decrease gradually from 5 to 25 phr. Tensile and flexural strength of composites increase gradually from 0 to 10 phr of pyrogenic silica, and then decrease gradually when the silica content is in excess of 10 phr. It was found that the optimum filler content is between 5 and 10 phr, which will provide pultruded parts with the best mechanical properties.

Postcure Temperature and Time Effect

The main purpose of postcuring is to ensure complete reaction and to drive off volatiles from the composites. In the pultrusion process, the monomer
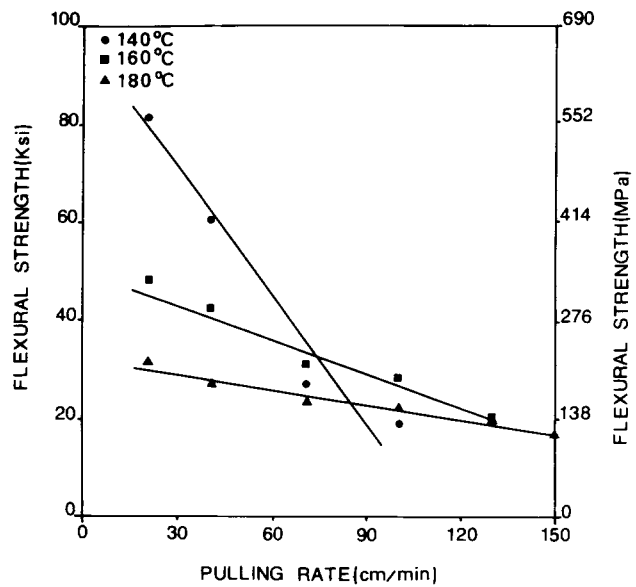

Figure 12 Flexural strength of pultruded glass-fiber-reinforced PMMA composites vs. pulling rate at various die temperatures: (●) 140°C; (■) 160°C; (▲) 180°C.

polymerizes in the die in a short time, but the polymerization may not be completed. Postcuring will help unreacted prepolymer to react to a higher degree; hence, postcuring the pultruded glass reinforced composites will increase the molecular weight of polymer matrix and may improve mechanical properties of composites material. Table IV summarizes the weight average molecular weight (M_w)
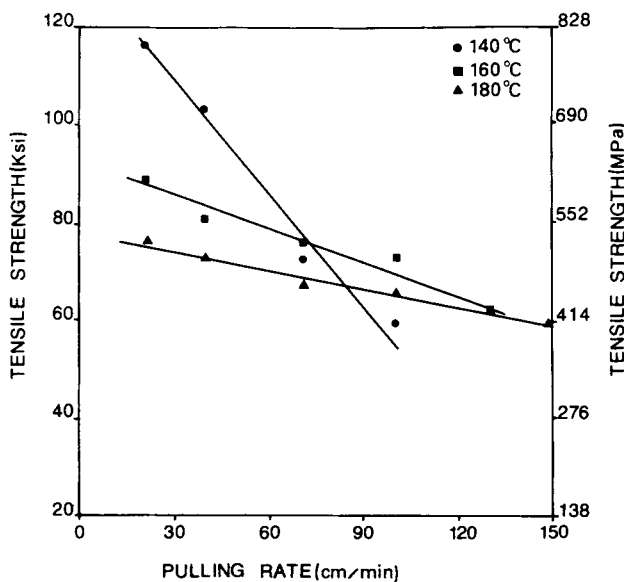

Figure 11 Tensile strength of pultruded glass-fiber-reinforced PMMA composites vs. pulling rate at various die temperatures: (●) 140°C; (■) 160°C; (▲) 180°C.
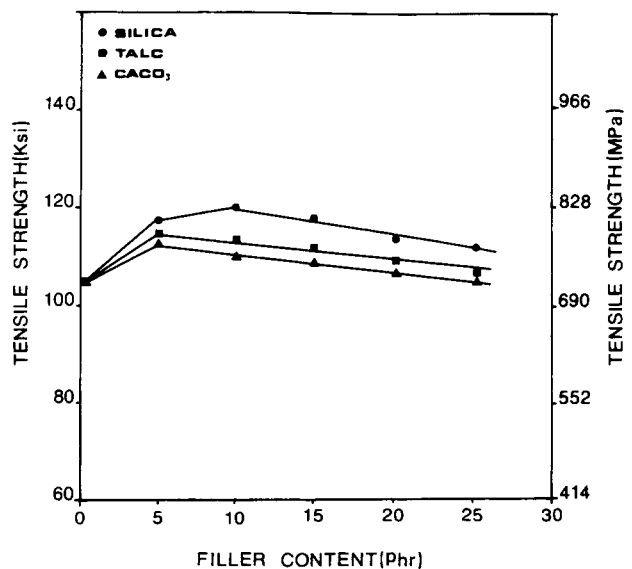

Figure 13 Tensile strength of pultruded glass-fiber-reinforced PMMA composites vs. filler content. Filler type: (●) silica; (■) talc; (▲) CaCO₃.

Table IV The Weight Average Molecular Weights (M_w) of Pultruded Glass Fiber-Reinforced PMMA Composites versus Postcure Time at various Temperatures

Postcure Temperature (°C)	Postcure Time (h)				
	0	4	8	12	16
			M_w (10^6)		
80	1.65	1.70	1.73	1.78	1.81
100	1.65	1.97	2.06	2.10	2.04
130	1.65	2.01	2.14	2.11	—

versus postcure time at various temperatures. One can see M_w increasing with postcure time and temperature.

Figure 15 illustrates the flexural strength of pultruded glass-fiber-reinforced PMMA composites versus postcure time at various temperatures. From these results one can see that the flexural strengths of composites were improved by postcuring at 80, 90, 100, and 130°C. Although the postcuring can improve the mechanical properties, from this figure one can observe that the composites begin to degrade after 12 h at postcuring temperature 130°C, and 16 h at 100°C. From Table IV, one can observe that the M_w began to decrease when the composites were treated by postcuring after 12 h at 130°C and 16 h at 100°C, and the flexural strength was reduced.
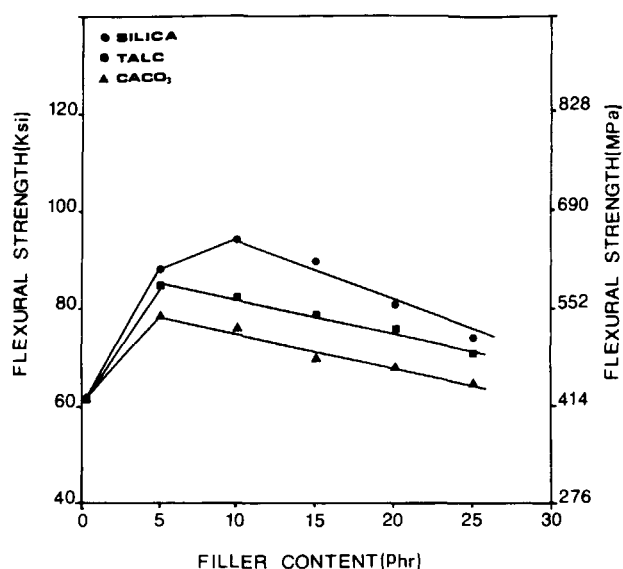

Figure 14 Flexural strength of pultruded glass-fiber-reinforced PMMA composites vs. filler content. Filler type: (●) silica; (■) talc; (▲) CaCO₃.
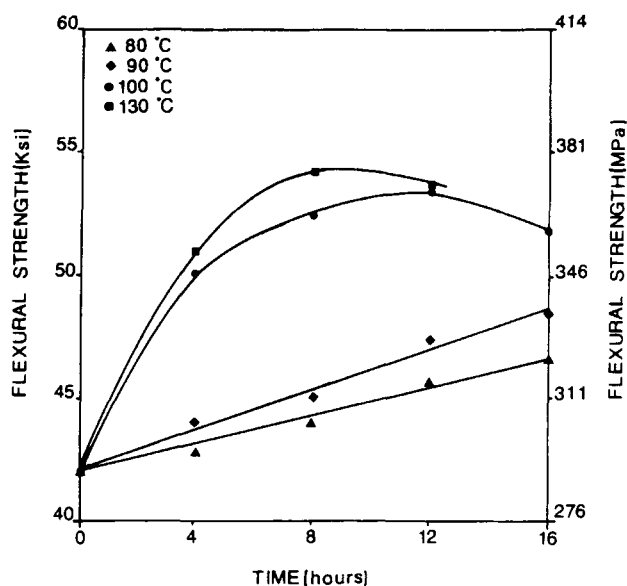

Figure 15 Flexural strength of pultruded glass-fiber-reinforced PMMA composites vs. postcure time at various postcure temperatures (°C): (▲) 80; (♦) 90; (●) 100; (■) 130.

CONCLUSIONS

A novel thermoplastic PMMA resin system was developed for the pultrusion process. The pultruded PMMA products were investigated. From SEM photographs and mechanical properties tests, good fiber wet-out by the PMMA matrix was confirmed. It was found that fiber bundles were distributed evenly in the PMMA matrix. From ^{1}H-NMR, GPC, and Brookfield viscometer study, the optimum conversion rate, weight average molecular weight, and viscosity of MMA prepolymer synthesized in this study were: 20%, 1200–1500 and 900–1200 cps (at 25°C), respectively.

A filler content of 5–10 phr can be used to fabricate pultruded parts having optimum mechanical properties and the least part shrinkage. The optimum pulling rate for pultruding fiber-reinforced PMMA composite was from 40 to 100 cm/min. From DSC diagrams, molecular weight measurement and the rule of polymerization rate, suitable pultrusion die temperatures were found to be in the range of 140–180°C. The postcuring process can improve the mechanical properties of pultruded product.

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