Pultruded Fiber Reinforced Blocked Polyurethane (PU) Composites. II. Processing Variables and Dynamic Mechanical Properties

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SYNOPSIS

Unidirectional fiber reinforced blocked polyurethane (PU) composites have been prepared by the pultrusion process. The effects of processing variables on the mechanical properties and dynamic mechanical properties of fiber reinforced PU composites by pultrusion have been studied. The processing variables investigated included pulling rate (in-line speed), die temperature, postcure time and temperature, and filler type and content. The dynamic mechanical properties of the composites produced by the process were studied utilizing dynamic mechanical spectrometer. Results show that the composites possessed various optimum pulling rates at different die temperatures. From the DSC data analysis, swelling ratio, and mechanical properties, the optimum die temperature was determined. It was found that the mechanical properties increase with filler content for various types of filler. The increasing of mechanical properties depends on the optimum postcure temperature and time. However, the properties decreased for longer postcure times since the composite materials were degraded. The glass-transition temperature (T_g) increased slightly and the damping peak (tan δ) was broadened due to fiber reinforcement. The dynamic mechanical moduli (G', G'') of pultruded PU composites are apparently higher than those of the matrices. The moduli (G', G'') increase with increasing fiber and filler content, and the damping peak becomes broad. Effect of postcuring on the degree of crosslinking, T_g, and dynamic modulus will be discussed.

INTRODUCTION

Pultrusion is an automatic process for manufacturing continuous and constant cross-sectional profile composite materials. The annual growth rate of this process was about 17–20% over the past decade.[1] Most literature published[2-8] illustrates the applications and some aspects of pultruded products instead of studying the resin formulations, processing variables, and relationship between them. A number of papers have been published which emphasise the traditional thermoset resins such as unsaturated polyester, epoxy, and phenolic.[9-16] Recently, new resin formulations and processing variables for pultruded composites have been studied.[17,18] In order to obtain the best mechanical properties, and the optimum process condition for pultrusion, the processing variables have to be investigated to optimize the pultrusion process. In order to investigate the best structural application of pultruded composites, the dynamic mechanical properties of composites should be studied.[19]

In this study, a blocked NCO-terminated PU prepolymer with a suitable viscosity range (500–2000 cps) was first synthesized from its basic materials (see Part I), and then was reacted with chain extender, cycloaliphatic diamine (Laromin C260). The prepolymer with chain extender was used directly and polymerized in the die. This paper investigates the effect of processing variables (pulling rate, die temperature, postcure temperature and time, filler type, and content) on the mechanical properties of pultruded composites, and studies the dynamic mechanical properties of composites.

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EXPERIMENTAL

Materials

A blocked NCO-terminated PU prepolymer synthesized in this study has been described in Part I. The chain extender (curing agent) used was cycloaliphatic diamine (Laromin C260) and was supplied by the Shell Chemical Co., USA, which has a specific gravity of 0.94–0.95, an equivalent weight with respect to active hydrogen of 60. The continuous E-glass fiber roving reinforcement used in this research was 764-NT-218 and was supplied by the PPG Co., USA, which has a filament diameter of 13.1 μm, a tensile strength of 206 ksi (1421 MPa) and a density of 2.54 g cm^{-3}. Two fillers were used in this study, calcium carbonate (Yin Chin Co., Taiwan, ROC), which has a density of 2.7 g cm^{-3}, a particle size of 350 mesh, 2.02 μm, and mica (Charles Star Enterprise Co., Taiwan, ROC), which has a particle size of 325 mesh.

Apparatus

The pultrusion machine used was described in Part I. Resin viscosities were measured with a Brookfield RVF model viscometer. The DSC (differential scanning calorimeter) used was a Model 910 (Du Pont Co., USA). The universal material testing machine used was an Instron 4201 (Instron Co., USA). A Rheometrics dynamic spectrometer, Model 800, was used to measure the dynamic mechanical properties.

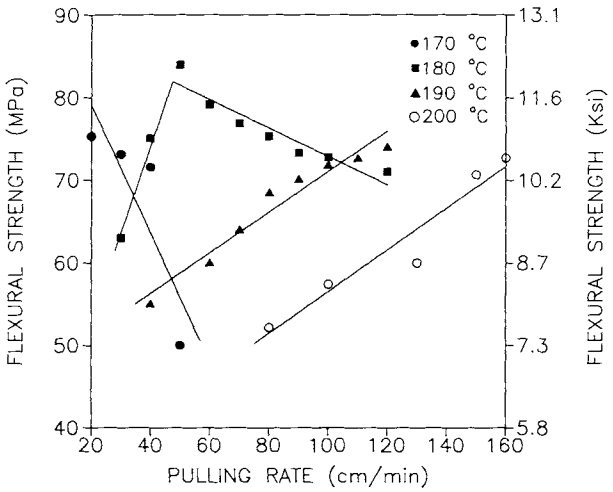

Figure 1 Flexural strength of pultruded glass fiber reinforced PU composites versus pulling rate at various die temperatures (°C): (●) 170; (■) 180; (▲) 190; (○) 200.

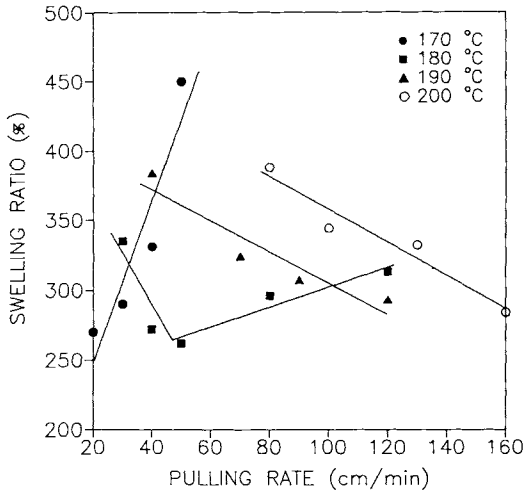

Figure 2 Swelling ratio of pultruded glass fiber reinforced PU composites versus pulling rate at various die temperatures (°C): (●) 170; (■) 180; (▲) 190; (○) 200.

Property Measurements

Flexural strength was measured following ASTM D-790. The sample dimensions were 12.7 × 1.25 × 0.2 cm (length × width × thickness), the span was 9 cm and crosshead speed was 2 mm/min. The swelling ratio q was defined as the ratio of the volume of the swollen composites to that of the unswollen composites. The sample dimensions of 3.0 × 1.25 × 0.2 cm were weighed and then placed in chloroform in covered Petri dishes at room temperature. They were removed after 72 h, blotted dry with absorbent tissue as carefully and quickly as possible, and reweighed. The swelling ratio was obtained by means of the following equation[20,21]:

$$q = V/V_0 = 1 + (W - W_0)D_0/W_0D_s \quad (1)$$

where V_0 is the volume of the unswollen pultruded composite, V is the volume of the swollen pultruded composite, W_0 is the weight of the unswollen pultruded composite, W is the weight of the swollen pultruded composite, D_0 is the density of pultruded composite, and D_s is the density of solvent (chloroform). The dynamic mechanical properties were measured by Rheometrics dynamic spectrometer. The sample dimensions were 5.0 × 1.25 × 0.2 cm.

RESULTS AND DISCUSSION

Processing Variables

Pulling Rate. Figure 1 shows the effect of pulling rate on the flexural strength of pultruded glass fiber

Table I DSC Data of Blocked NCO-Terminated PU Prepolymer with Cycloaliphatic Diamine for Dynamic Scanning

Scan Rate (°C/min)	Peak Start Temp (°C)	Peak Onset Temp (°C)	Peak Max Temp (°C)	Peak End Temp (°C)	ΔH (J/g)
10	132	143	170	181	24.2
20	138	153	180	194	22.9
30	141	155	184	199	21.5
40	146	160	190	211	20.6

reinforced PU composites at die temperatures of 170, 180, 190, and 200°C, respectively. 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. From Figure 1, one can observe that when the die temperature was 170°C, the lower the pulling rate, the better the mechanical properties. When the pulling rate is higher than 50 cm/min at the die temperature of 180°C, the mechanical properties increase with decreasing pulling rate. However, when the pulling rate is lower than 50 cm/min, the lower the pulling rate, the worse the mechanical properties. The pultruded fiber reinforced PU composites began to degrade when the pulling rate is lower than 50 cm/min and the die temperature is over 180°C. The fiber content of pultruded composites at various pulling rates is 76.5–77.5 wt %. It is almost constant at various pulling rates in this study.

As shown in Figure 1, when the pulling rate is lower than 120 cm/min at die temperature of 190°C and lower than 160 cm/min at die temperature of 200°C, the mechanical properties increase with increasing pulling rate. When the pulling rates are lower than 120 and 160 cm/min at die temperatures of 190 and 200°C respectively, the pultruded fiber reinforced PU 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 increased with decreasing swelling ratio. The higher the degree of degradation of these composites, the greater the swelling ratio. Figure 2 shows the effect of pulling rate on the swelling ratio of pultruded glass fiber reinforced PU composites at die temperatures of 170, 180, 190, and 200°C, respectively. Comparing Figure 2 with Figure 1, one can find that the mechanical properties of pultruded glass fiber reinforced PU composites increased with decreasing swelling ratio.

From the above explanations, the optimum pull-

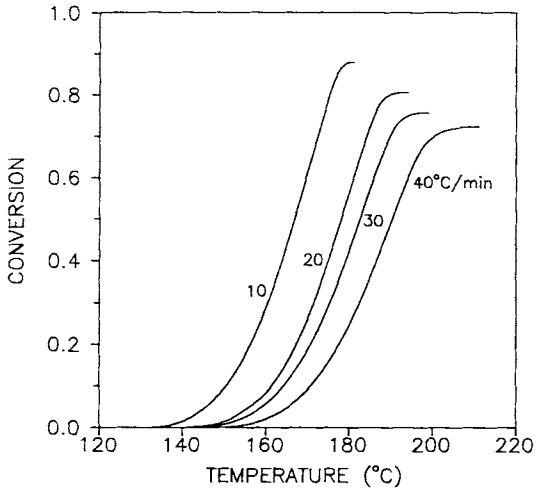

Figure 3 Conversion (extent of reaction) vs. temperature of blocked NCO-terminated PU prepolymer with cycloaliphatic diamine for dynamic DSC.

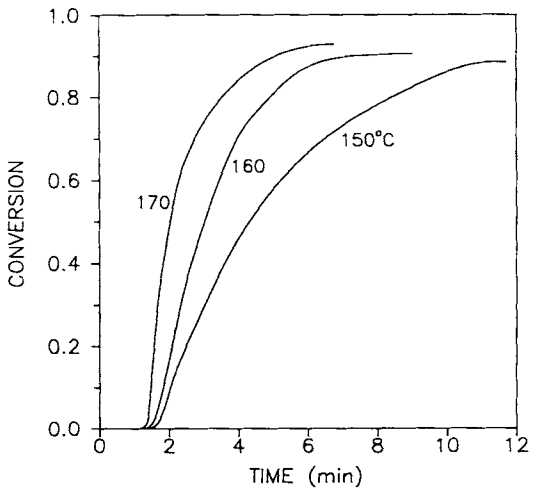

Figure 4 Conversion (extent of reaction) vs. time of blocked NCO-terminated PU prepolymer with cycloaliphatic diamine for isothermal DSC.

ing rates are found to be 20, 50, 120, and 160 cm/min corresponding to the die temperatures of 170, 180, 190, and 200°C, respectively, in this study.

Die Temperature. The optimum die temperature was determined by differential scanning calorimetry. Five to 10 mg of blocked NCO-terminated PU prepolymer with cycloaliphatic diamine (Laromin C260) sample was placed in the DSC cell. Both dynamic scanning at 10, 20, 30, and 40°C/min and isothermal scanning at 150, 160, and 170°C were conducted. From the dynamic DSC results shown in Table I, one can see that the exothermic peak reached a maximum at 170, 180, 184, and 190°C, and the total heats generated during the polymerization were measured as 24.2, 22.9, 21.5, and 20.6 J/g for 10, 20, 30, and 40°C/min scanning, respectively. The conversion of reaction (extent of reaction) versus temperature for a series of dynamic DSC scanning is shown in Figure 3, where a value for the total heat of reaction of 28.44 J/g from the 5°C/min scanning was used for all the curves. As shown in Figure 3, the final plateau value for the conversion decreases with increasing scanning rates. Figure 4 shows the conversion versus time for a series of isothermal DSC scanning. From Figure 3, a high conversion of reaction (>70%) was measured when the reaction temperature was higher than 170, 184, 190, and 200°C for 10, 20, 30, and 40°C/min scanning, respectively. As can be seen in Figure 4, a high conversion (>70%) was measured in a short time (<4 min) when the reaction temperature is higher than 170°C. From the above explanations, the die temperature should be higher than 170°C.

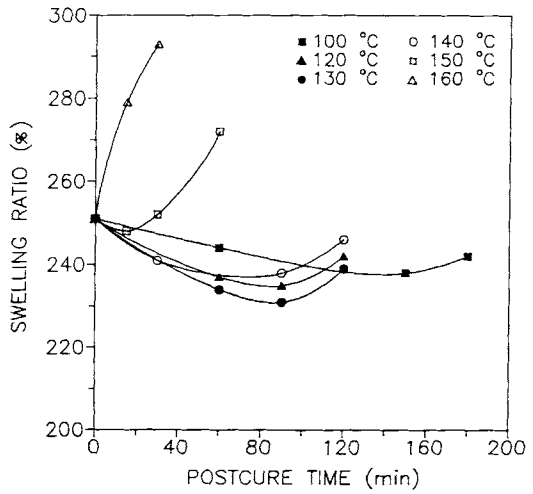

Figure 5 Swelling ratio of pultruded glass fiber reinforced PU composites versus postcure time at various postcure temperatures (°C): (■) 100; (▲) 120; (●) 130; (○) 140; (□) 150; (△) 160.

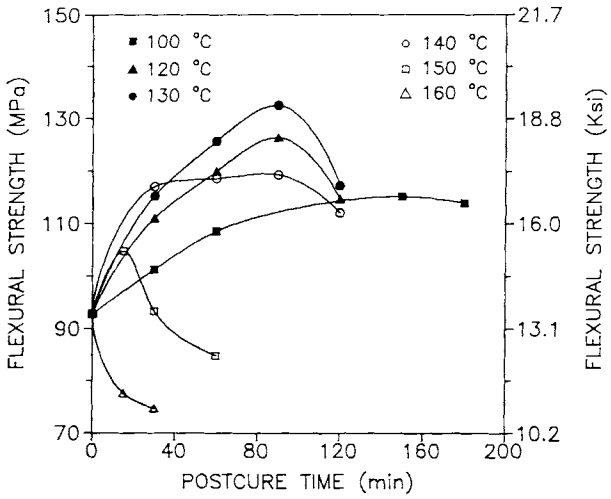

Figure 6 Flexural strength of pultruded glass fiber reinforced PU composites versus postcure time at various postcure temperatures (°C): (■) 100; (▲) 120; (●) 130; (○) 140; (□) 150; (△) 160.

As shown in Figure 1, it can be observed that when the die temperature was above 180°C, the lower the die temperature, the better the mechanical properties. Since the pultruded fiber reinforced PU composites begin to degrade at die temperatures over 180°C. The die temperature should not be higher than 200°C, otherwise the composites might be degraded. When the die temperature is lower than 180°C, the lower the die temperature, the worse the mechanical properties, since the degree of crosslinking was lower and swelling ratio was higher at low temperature as illustrated in Figure 2. However, when the pulling rate of glass fiber reinforced PU composites is lower than 35 cm/min, the mechanical properties increase with decreasing die temperature. The composites degrade when the pulling rate is lower than 35 cm/min at die temperatures lower than 180°C. However, the die temperature cannot be lower than 170°C; otherwise, the composites cannot be processed in a short time in the die.

Hence, from the DSC results, the study of mechanical properties and swelling ratio, one can observe that the suitable die temperature range in this study is between 170 and 200°C.

Postcure Temperature and Time. The main purpose of postcuring is to ensure complete reaction and to drive off volatiles from the composites. In a pultrusion process, the resin polymerizes in the die in a short time, but the polymerization may not be completed. Postcuring will cause the unreacted prepolymer to react to a higher degree. Hence, postcuring the pultruded glass reinforced composites will

Table II Viscosity vs. Temperature of Blocked NCO-Terminated PU Prepolymer with Cycloaliphatic Diamine (Laromin C260) with Various Types of Filler Contents

		Viscosity (cps)							
		$CaCO_3$ (phr)				Mica (phr)			
Temp (°C)	Blank	10	20	30	40	10	20	30	40
50	1780	1952	2218	2495	2905	2183	3450	6044	10381
55	1240	1369	1555	1675	1970	1533	2424	3700	7713
60	885	966	1098	1200	1383	1108	1772	2780	4750
65	655	708	805	870	1008	838	1324	1860	3575
70	505	538	603	650	758	608	972	1450	2890
75	380	410	465	495	580	460	732	1140	1865
80	303	334	375	395	453	374	588	925	1505
85	248	268	302	318	375	300	478	752	1253

increase the degree of crosslinking (i.e., decrease the swelling ratio) of the polymer matrix and may improve the mechanical properties of composites material. Figure 5 shows the swelling ratios of pultruded glass fiber reinforced PU composites versus postcure time at various temperatures. One can observe that the swelling ratio increases with decreasing postcure time and temperature.

Figure 6 illustrates the flexural strength of pultruded glass fiber reinforced PU composites versus postcure time at various temperatures. From these results one can see that the flexural strength of composites were improved by postcuring at 100, 120, 130, 140, and 150°C. Properties were reduced when they were postcured above 160°C. However, when the postcure temperatures are below 130°C, the flexural strength of pultruded fiber reinforced PU composites increase with increasing postcure temperature. When the postcure temperatures are above 130°C, the mechanical properties of pultruded glass fiber reinforced PU composites decrease with increasing postcure temperature. Although the postcuring step may improve the mechanical properties, the composites begin to degrade after postcuring for 150, 90, 90, 90, and 15 min corresponding to the postcuring temperatures of 100, 120, 130, 140, and 150°C, respectively. The composites degrade significantly from the beginning of postcuring at 160°C; the mechanical properties were reduced. As shown in Figures 5 and 6, the higher the mechanical properties, the lower the swelling ratios.

Filler Type and Content. The purposes of add-

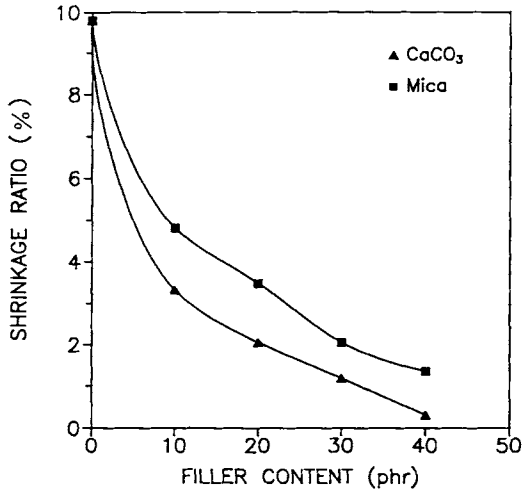

Figure 7 Shrinkage ratio of pultruded glass fiber reinforced PU composites versus various types of filler contents: (▲) $CaCO_3$; (■) Mica.

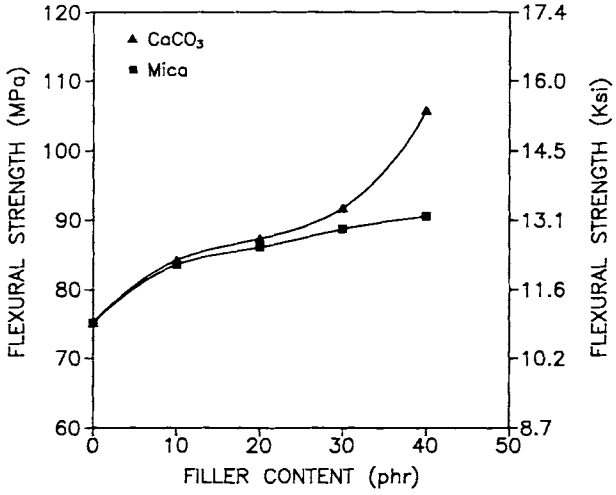

Figure 8 Flexural strength of pultruded glass fiber reinforced PU composites versus various types of filler contents: (▲) $CaCO_3$; (■) Mica.

ing fillers to the fiber reinforced pultruded composites are the following: (1) to reduce the cost of materials, (2) to reduce the shrinkage of pultruded parts, and (3) to improve the mechanical properties and surface of finished product. In a pultrusion process, if without filler, the surfaces of pultruded composites may become coarse and the mechanical properties may be decreased.

In this study, two fillers, calcium carbonate and mica, were added to the pultruded glass fiber reinforced PU composites. Table II summarizes the viscosities of resin with calcium carbonate and mica versus temperature. It is shown that viscosities of resin containing calcium carbonate (0–40 phr) and mica (0–20 phr) maintained at 500–2000 cps in the impregnation tank at 55–70°C. When the mica content was increased from 30 to 40 phr, the viscosity increased rapidly. Consequently, the temperature of the impregnation tank has to be raised to 70–85°C when 30 phr mica is added, or raised to 75–85°C when 40 phr mica is added.

Figure 7 shows the change of shrinkage ratio of pultruded glass fiber reinforced PU composites with various filler types and contents. The shrinkage ratio of composites decreased with increasing filler contents, and the shrinkage ratios of calcium carbonate filled composites were lower than those filled with mica.

Figure 8 shows the change of flexural strength of pultruded glass fiber reinforced PU with various filler types and contents. It is shown that the flexural strength of composites increases gradually with increasing mica content. The mechanical properties increase gradually from 0 to 30 phr of calcium carbonate, and increase sharply from 30 to 40 phr of calcium carbonate. The improvements of mechanical properties of composites with calcium carbonate are superior to those with mica.

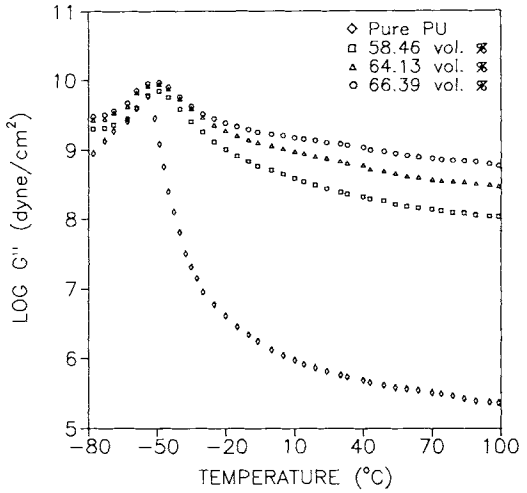

Figure 10 Dynamic shear loss modulus (G'') vs. temperature of pultruded GF/PU composite at various fiber volume contents (%): (◇) pure PU; (□) 58.46; (△) 64.13; (○) 66.39.

Dynamic Mechanical Properties

The dynamic mechanical behavior of composites is of great interest and important in structural appli-

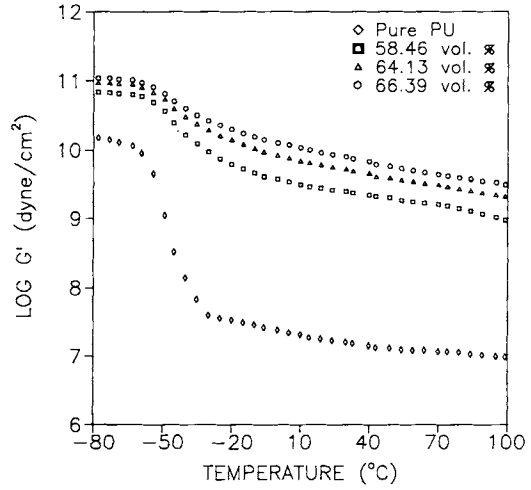

Figure 9 Dynamic shear storage modulus (G') vs. temperature of pultruded GF/PU composite at various fiber volume contents (%): (◇) pure PU; (□) 58.46; (△) 64.13; (○) 66.39.

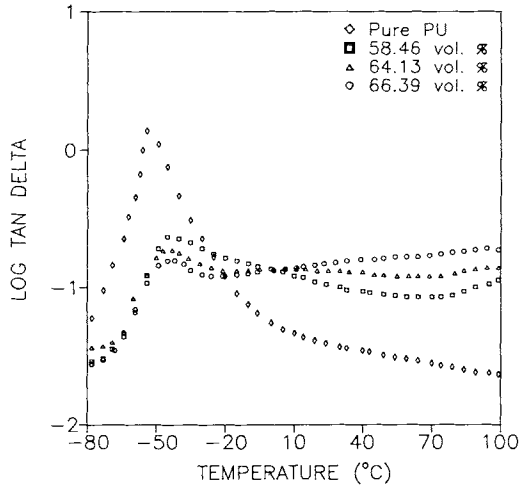

Figure 11 Dynamic tan δ (damping) vs. temperature of pultruded GF/PU composite at various fiber volume contents (%): (◇) pure PU; (□) 58.46; (△) 64.13; (○) 66.39.

cation, and is very sensitive to the processing conditions. An unreinforced polymers and an incomplete polymerization composites still show good appearance and reasonable integrity, but the dynamic mechanical behavior would be quite different from that of reinforced polymers and well-polymerized composites.

Figures 9–11 show the dynamic mechanical spectra of pure PU and pultruded GF/PU composite in the range of −80 to 100°C. From Figures 9 and 10, one can observe that the shear storage modulus (G') and loss modulus (G'') increased with increasing fiber content, and the dynamic modulus of pultruded composites increased significantly as compared with the PU matrices. From Figure 11, one can observe that the glass-transition temperature (T_g) of pure PU is −52.5°C; it is noteworthy that, in the presence of about 58–67 vol% glass fiber, the T_g in the composite occurred at a higher temperature (−45°C) and the damping peak becomes broad. Although the glass fiber is inert in this temperature range,[22] however, the dynamic mechanical properties of composite changed as compared with the matrix when the fibers are added to the PU matrix due to the effect of fiber–matrix interphase. The upshift of the glass-transition temperature, the broader damping peak and the increasing of the dynamic modulus are due to the bonding between matrix and fiber restricting the PU chain motion.

Figure 12 shows the dynamic shear storage and loss moduli (G', G'') versus temperature of pultruded GF/PU composites at various calcium carbonate contents. From this figure, the higher the calcium carbonate, the higher the G' and G''. Figure 13 shows that the damping peak versus temperature of pultruded GF/PU composite becomes broad with increasing calcium carbonate content; however, the glass-transition temperature does not shift to higher temperatures. The dynamic moduli increase with filler due to the composite structure becomes tighter when the filler is added.

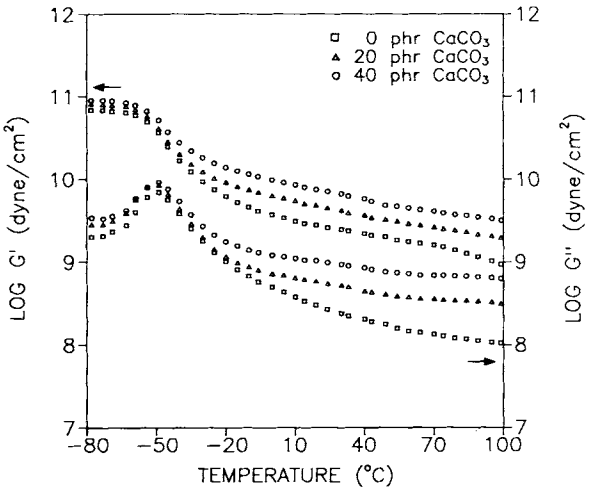

Figure 12 Dynamic shear storage and loss moduli (G', G'') vs. temperature of pultruded GF/PU composite at various $CaCO_3$ contents (phr): (□) 0; (△) 20; (○) 40.

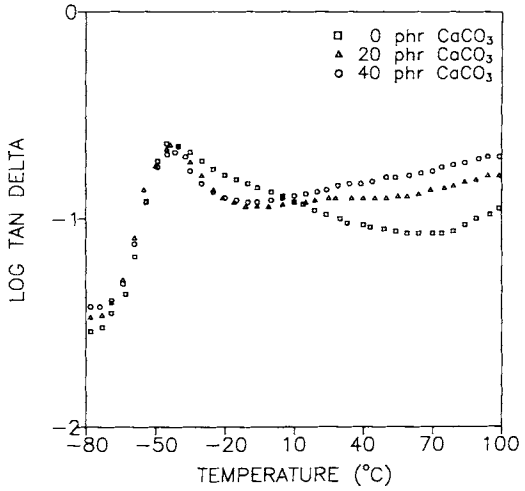

Figure 13 Dynamic tan δ (damping) vs. temperature of pultruded GF/PU composite at various $CaCO_3$ contents (phr): (□) 0; (△) 20; (○) 40.

Another important factor in determining the dynamic mechanical properties of material is the thermal history.[22] Thus, the original pultruded sample may show some differences in the spectra after postcure, since the degree of crosslinking of composite may be enhanced. Figures 14 and 15 show the change

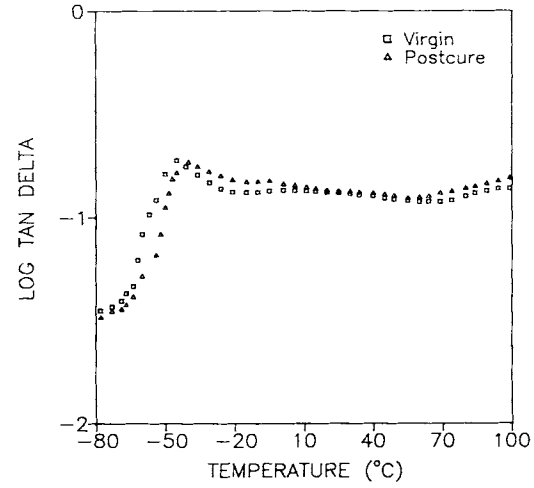

Figure 14 Dynamic tan δ (damping) vs. temperature of pultruded GF/PU composite: (□) virgin; (△) postcure.

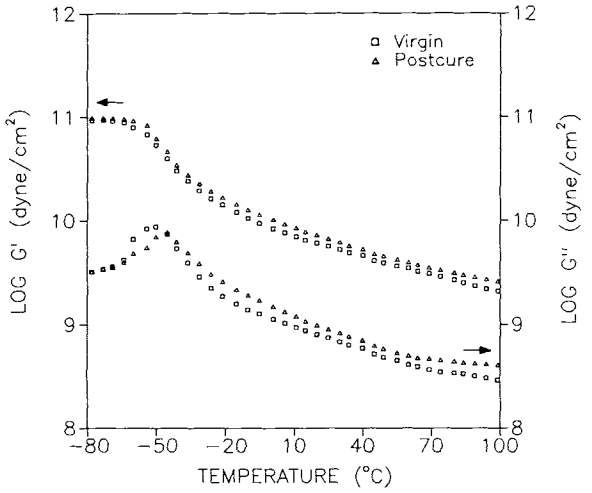

Figure 15 Dynamic shear storage and loss moduli (G', G'') vs. temperature of pultruded GF/PU composite: (□) virgin; (△) postcure.

of the dynamic mechanical properties of pultruded PU composite in the range of −80–100°C before and after postcuring at 120°C for 60 min. From Figure 14, it can be seen that the glass-transition temperature (T_g) shifts to higher temperatures after postcure. From Figure 15, the dynamic moduli (G', G'') increase dramatically above T_g since crosslinking shows a significant effect on the dynamic mechanical properties above T_g.[19] Results show the effect of postcuring on the shift of T_g and the increasing modulus due to the increase in degree of crosslinking. The higher degree of crosslinking makes the polymer chains entangle more tightly, thus the polymer chains cannot move easily. Dynamic mechanical property studies indicate that the polymerization was complete in the pultrusion process.[22]

CONCLUSIONS

A proprietary pultrusion process has been successfully applied to prepare unidirectional fiber reinforced blocked NCO-terminated PU composites. The effect of processing variables on the mechanical properties and dynamic mechanical properties of fiber reinforced PU composites by pultrusion has been studied.

The optimum pulling rates obtained in this study are 20, 50, 120, and 160 cm/min corresponding to die temperatures of 170, 180, 190, and 200°C, respectively. From the DSC data analysis, swelling ratios and mechanical property test, a suitable die temperature range found in this study is between 170 and 200°C. However, the die temperatures cannot be lower than 170°C; otherwise, the composites cannot be processed in a short time in the die. Furthermore, the die temperature cannot be higher than 200°C, or the composites may be degraded seriously.

It was also found that the postcuring process can improve the mechanical properties of pultruded parts at postcure temperatures of 100–150°C. The shrinkage ratio of composites decreased with increasing filler contents. The shrinkage ratios of composites containing calcium carbonate composites were lower than those containing mica. The mechanical properties of composites increase with increasing mica and calcium carbonate, and the improvements in mechanical properties containing calcium carbonate are superior to those containing mica.

The dynamic mechanical properties of the composites have been shown to resemble those of corresponding matrix materials. The slightly higher glass-transition temperature (T_g) and broader damping peak (tan δ) of pultruded composites were believed to be the result of fiber-introduced restraints as well as inhomogeneity as compared with the PU matrices. The dynamic moduli (G', G'') of pultruded PU composites are apparently higher than those of the matrices. The upshift of the glass-transition temperature, the broader damping peak and the increasing of the dynamic modulus are due to the bonding between matrix and fiber restricted the PU chain motion. The moduli (G', G'') increased with increasing the fiber and filler content, and the damping peak becomes broad. Postcuring process can enhance the degree of crosslinking of composites. The dynamic moduli increase dramatically above T_g, and T_g shifts to higher temperatures.

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