Pultruded Fiber-Reinforced Poly(methyl Methacrylate) Composites. II. Static and Dynamic Mechanical Properties, Environmental Effect, and Postformability

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SYNOPSIS

This paper presents a novel process developed to manufacture poly(methyl methacrylate) (PMMA) pultruded composite. The mechanical, thermal, and dynamic mechanical properties, environmental effect, postformability of various fiber (glass, carbon, and Kevlar 49 aramid fiber) reinforced pultruded PMMA composites have been studied. Results show mechanical properties (i.e., tensile strength, specific tensile strength, tensile modulus, and specific flexural strength) and thermal properties (HDT) increase with fiber content. Kevlar fiber/PMMA composites possess the highest specific tensile strength and HDT, carbon fiber/PMMA composites show the highest tensile strength and tensile modulus, and glass fiber/PMMA composites show the highest specific flexural strength. Pultruded glass-fiber-reinforced PMMA composites exhibit good weather resistance. These composite materials can be postformed by thermoforming under pressure, and mechanical properties of postformed products can be improved. The dynamic shear storage and loss modulus (G', G'') of pultruded glass-fiber-reinforced PMMA composites increased with decreasing pulling rate, and their shear storage moduli are higher than those of pultruded Nylon 6 and polyester composites.

INTRODUCTION

The pultrusion process has grown very rapidly in the past decade due to the development of materials and processing techniques.[1] One of the major advantages of the process is its continuous nature, which, in principle, may enable a high degree of automation. The current emphasis on automation and advanced manufacturing techniques has, therefore, resulted in an increased interest in the process. Nevertheless, the matrix used in pultrusion has been associated exclusively with thermosets, such as unsaturated polyester, vinyl ester, phenolic, and epoxy resin.[2-10]

Basically, thermoset pultruded products have some disadvantages, such as brittleness, and cannot be reshaped. Material handling of thermoset resins is very tedious since these materials have a limited shelf-life and are often stored at very low temperature. Quality control is another cost factor with thermoset resin since each batch from the manufacturer has to be inspected before mixing and each formulation must be matched to previous batches.[11] Consequently, composite fabricators are researching thermoplastic matrix materials as replacements.

Thermoplastic materials show the potential for high-speed, low tooling cost, and a short cycle time process. Substantial cost reductions can also be realized due to their unlimited shelf life, reduced scrap and waste (due to the recyclability of the thermoplastic material), ease of repair, and the ability to be welded or fused together.[12-16] Thermoplastic composite material provides the opportunity for developing an entirely new era of pultruded composite profiles and structures.[17]

In this study, poly(methyl methacrylate) (PMMA) thermoplastic resin and various fibers have been used in the pultrusion process. This paper presents the dynamic mechanical properties, environmental effect, postformability, and the mechan-

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ical properties of pultruded glass fiber, carbon fiber, and Kevlar fiber reinforced PMMA composites.

EXPERIMENTAL

Materials

Table I summarizes the materials used in this study which include methyl methacrylate monomer, initiator, glass fiber, carbon fiber, Kevlar 49 aramid fiber, and MMA prepolymer synthesized in this study.

Apparatus

The pultrusion machine has been described in Part I. The surfaces of the stainless steel die have been treated by chrome plating. A universal material testing machine was used for 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 heat deflection temperature tester used was a Fine-Gang Type, (Tinius Olsen Testing Machine Co., U.S.A.). The SEM (Scanning Electron Microscope) used was a S-570 (Hitachi Co., Japan). The RDS (Rheometric dynamic spectrometer) utilized was a Model 800 (Rheometrics Inc., U.S.A.).

Property Measurements

Specific tensile strength and tensile modulus were measured following the specification of ASTM D-3039. The sample dimensions were 22.9 × 1.25 × 0.319 cm and the crosshead speed was 2.5 cm/min. Specific flexural strength was measured following ASTM D-790. The sample dimensions were 12.7 × 1.25 × 0.319 cm, the span was 9 cm, and the crosshead speed was 2 mm/min. Notched Izod impact strength was measured following ASTM D-256. The sample dimensions were 6.35 × 1.25 × 0.319 cm. Heat deflection temperature was measured following ASTM D-648. The sample dimensions were 12.5 × 1.25 × 0.319 cm.

RESULTS AND DISCUSSION

Effect of Type and Content of Fiber Reinforcements on the Mechanical Properties of Pultruded PMMA Composites

In order to investigate the effect of type and content of fiber reinforcements on the properties of pultruded PMMA composites, glass fiber (GF), carbon fiber (CF), and Kevlar fiber (KF) reinforced PMMA composites (GF/PMMA, CF/PMMA, and KF/PMMA) with various fiber contents were fabricated in this study. Specific tensile, flexural strength and modulus, and HDT of composites were measured.

Tensile Strength, Specific Tensile Strength, and Tensile Modulus

Figures 1–3 illustrate the tensile strength, specific tensile strength, and tensile modulus of pultruded glass fiber, carbon fiber, and Kevlar fiber reinforced PMMA composites with various fiber contents. It is shown that the tensile strength, specific tensile strength, and tensile modulus increased with fiber volume content and a linear relationship exists. CF/PMMA composites possess the highest tensile strength and tensile modulus, while GF/PMMA composites are the lowest. The specific tensile strength of KF/PMMA composite is the highest, while that of GF/PMMA composite is the lowest among the composites studied.

Specific Flexural Strength

The effect of fiber volume content on specific flexural strength is shown in Figure 4. It was found that the

Table I Materials Used for This Study

Material	Specification	Supplier
Monomer	Methyl methacrylate (purified industry grade)	Kaohsiung Monomer Co., Taiwan, R.O.C.
Resin	MMA prepolymer (M_w = 1200)	Synthesized in this study
Initiator	Benzoyl peroxide (BPO) (guaranteed reagent)	Kanto Chemical Co., Japan
Fiber	Glass fiber (E-glass), 764-NT-218, diameter = 13.1 μm Carbon fiber, HT-12000, diameter = 7.0 μm Kevlar fiber, K-49, diameter = 11.9 μm	PPG Co., U.S.A. Toho Co., Japan DuPont Co., U.S.A.

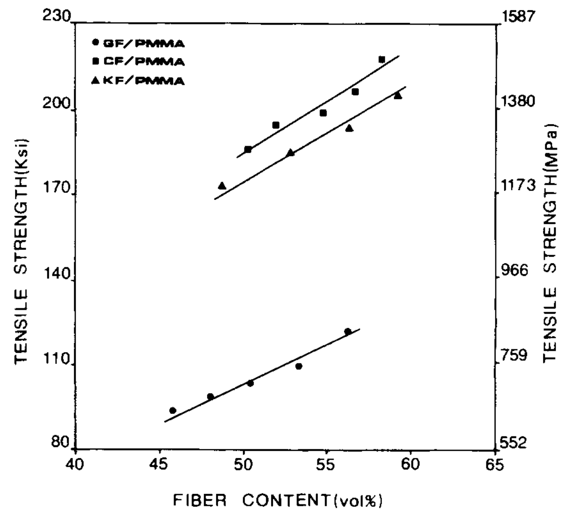

Figure 1 Tensile strength vs. fiber volume content of pultruded glass fiber (●), carbon fiber (■), and Kevlar fiber (▲) reinforced PMMA composites.

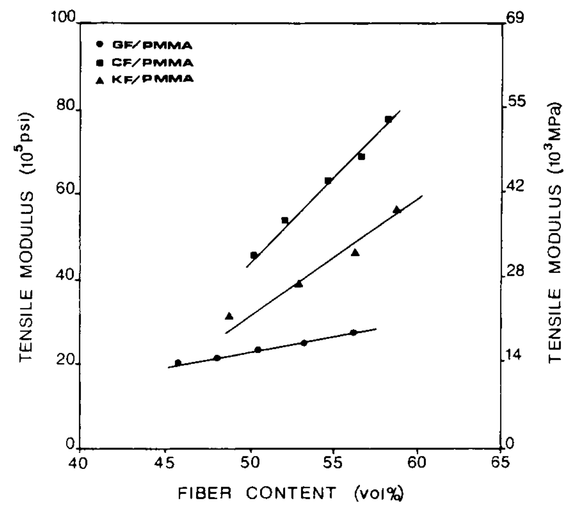

Figure 3 Tensile modulus vs. fiber volume content of pultruded glass fiber (●), carbon fiber (■), and Kevlar fiber (▲) reinforced PMMA composites.

higher the fiber volume content, the higher the specific flexural strength. GF/PMMA shows the highest specific flexural strength followed by CF/PMMA and KF/PMMA.

Heat Deflection Temperature (HDT)

Since PMMA is an amorphous polymer, the HDT of pultruded PMMA composite increased only slightly. The HDT of neat PMMA resin is 75–80°C, the HDT of pultruded fiber-reinforced PMMA is 95–120°C. Figure 5 illustrates heat deflection temperature (HDT) versus fiber volume content of pultruded glass fiber, carbon fiber, and Kevlar 49 fiber reinforced PMMA composites. HDT increases with increasing fiber content. The significant increase in HDT is due to the increase in modulus.[18]

Figure 5 shows that KF/PMMA composites possess the highest HDT among the composites studied; however, the heat resistance of Kevlar 49 fiber is the least among the three fibers investigated. This can be explained from observation of the experi-

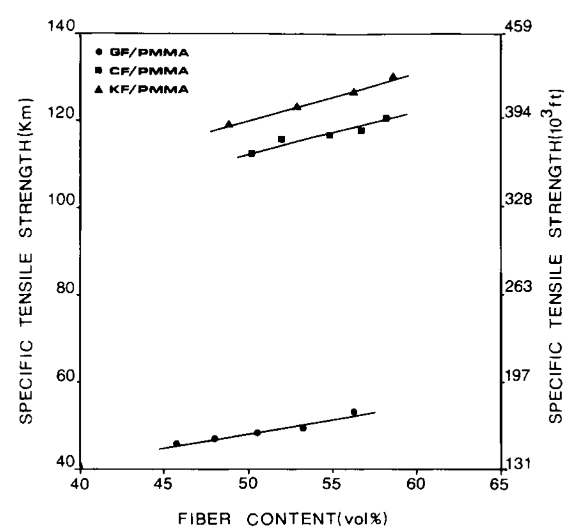

Figure 2 Specific tensile strength vs. fiber volume content of pultruded glass fiber (●), carbon fiber (■), and Kevlar fiber (▲) reinforced PMMA composites.

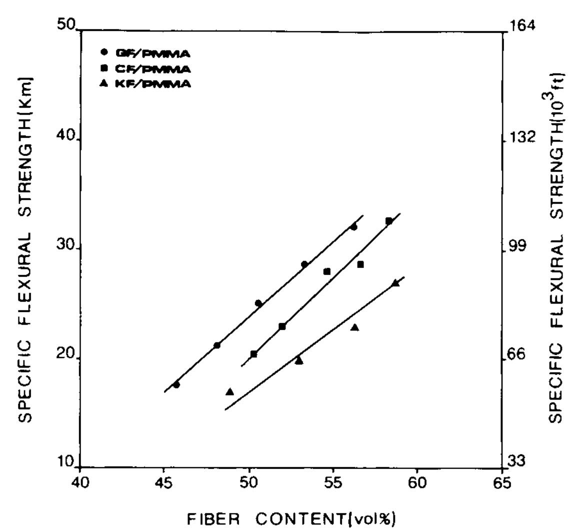

Figure 4 Specific flexural strength vs. fiber volume content of pultruded glass fiber (●), carbon fiber (■), and Kevlar fiber (▲) reinforced PMMA composites.

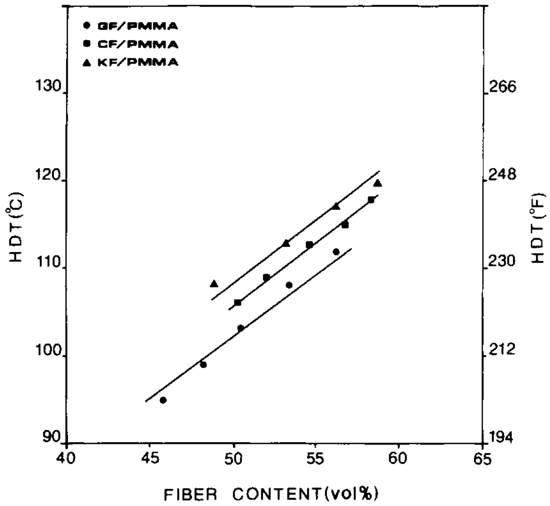

Figure 5 HDT vs. fiber volume content of pultruded glass fiber (●), carbon fiber (■), and Kevlar fiber (▲) reinforced PMMA composites.

mental results and theoretical background. HDT (according to ASTM D-648) is defined as the temperature at which the test specimen shows a deflection of 0.25 mm under 264 psi loading. The deflection indicator was adjusted to zero before the test. During the heating process, the composite deflection is the result of two forces that are opposite in direction. The first one is an upward stress due to thermal expansion of the composite; the second is a downward loading stress. At the beginning of the test, the downward loading stress is less than the upward thermal expansion stress; hence, the deflection indicator shows a "negative" indication. The radial thermal expansion coefficient of Kevlar fiber is quite different from carbon and glass fiber[19] (see Table II). Hence, the upward thermal expansion stress of KF/PMMA is larger than those of CF/PMMA and GF/PMMA. As the testing temperature is elevated gradually, the downward loading stress becomes more significant. An equilibrium temperature will be reached, where the downward loading stress is equal to the upward thermal expansion stress and the indicator will go back to zero again. From experimental observation, the equilibrium temperatures of different fiber-reinforced PMMA composites are shown in Table II. When the testing temperature is above the equilibrium temperature, the downward deflection of the composite becomes very significant. Results show that KF/PMMA composites possess the highest HDT, followed by CF/PMMA and GF/PMMA.

Postformability

PMMA pultruded strip was cut into a suitable length and placed in a heated mold (at 190°C, 1000 psi) for 10 min, and then was cooled. Properties of postformed products are shown in Table III. One can observe that the mechanical and thermal properties of postformed pultruded products increased obviously. The reasons for the increase of mechanical and thermal properties are that the composites bond closely between fiber and PMMA matrix, and void content of composites decreased after compression molding. Table IV summarizes the void content of pultruded products and postformed products at various glass fiber contents. It is shown that the void content apparently decreased after postforming. This demonstrates that the PMMA pultruded products can be postformed or reshaped by using heat and pressure. This is one of the major advantages of thermoplastic pultruded products.

Environmental Effect

In this study, pultruded glass-fiber-reinforced PMMA composites were exposed to environments of 85% RH and 35, 60, 70 and 80°C. Figures 6 and 7 show the gradual decline of flexural strength and notched Izod impact strength of pultruded glass-fiber-reinforced PMMA composites when exposed to 85% RH and 60, 70, and 80°C for 135 days in a weathering chamber. The retention of flexural strength and notched Izod impact strength were 88 and 82%, respectively. Figures 8 and 9 summarize the mechanical and thermal properties of pultruded glass-fiber-reinforced PMMA composites versus exposure time up to 6 months at 85% RH and 35°C in weathering chamber. Retentions of tensile

Table II The Thermal Properties of Various Fibers and Their Reinforced PMMA Composites

Fiber	RTE (10^{-6}cm/cm °C)[a]	ETP (°C)[b]
Glass fiber	7.2	65 (56.1 vol % GF)
Carbon fiber	16.8	71 (56.5 vol % CF)
Kevlar fiber	59.4	88 (56.1 vol % KF)

[a] RTE = the radial thermal expansion coefficients of fiber.
[b] ETP = the equilibrium temperature of pultruded fiber reinforced PMMA composite.

Table III Properties Comparison between Pultruded and Pultruded/Postformed Products among Glass Fiber (GF), Carbon Fiber (CF), and Kevlar Fiber (KF) Reinforced PMMA Composites

	GF/PMMA		CF/PMMA		KF/PMMA	
	Pu[a]	Pu/PF[b]	Pu[a]	Pu/PF[b]	Pu[a]	Pu/PF[b]
Tensile strength MPa	848	1035	1435	1662	1345	1621
(ksi)	(123)	(150)	(208)	(241)	(195)	(235)
Flexural strength MPa	579	862	366	524	248	345
(ksi)	(84)	(125)	(53)	(76)	(36)	(50)
Notched Izod impact kJ/M	2.0	2.2	1.4	1.7	2.4	2.8
(ft-lb/in.)	(38)	(41)	(26)	(32)	(45)	(53)
HDT °C	108	110	113	116	117	119
(°F)	(226)	(230)	(235)	(241)	(243)	(247)

[a] Pu = pultrusion.
[b] Pu/PF = pultrusion/postforming.

strength, tensile modulus, and notched Izod impact strength are more than 85%, while flexural strength, flexural modulus, and HDT are retained more than 95%. This indicates that the pultruded composites should show good weather resistance.

When composites are exposed to hygrothermal condition, moisture, and temperature fluctuation will cause degradation and the bonding between fiber and matrix may be destroyed. The SEM photographs of fracture surface of pultruded glass-fiber-reinforced PMMA composites are shown in Figures 10(a)-(d). One can observe that the interfacial bonding between glass fiber and PMMA resin were destroyed increasingly with time in 6 months under 85% RH and 35°C.

Properties Comparison of Pultruded Glass-Fiber-Reinforced PMMA Composites with Other Pultruded Composites

Tables V and VI show the properties of pultruded glass-fiber- and carbon-fiber-reinforced PMMA composites and other pultruded thermoplastic composites (nylon 6[22], PPS, ABS[22]) and thermoset composites (unsaturated polyester, phenolic[21], epoxy). They are summarized as follows:

Table IV The Void Content of Glass-Fiber-Reinforced PMMA Composites by Pultrusion and Pultrusion/Postforming

Fiber Content (vol %)	Void Content (%) Pultrusion	Void Content (%) Pultrusion/ Postforming
48.0	5.16	1.02
50.4	4.81	1.06
53.1	4.71	1.05
56.1	4.05	1.15

Tensile Strength

The pultruded GF/PMMA and GF/nylon 6 composites possess the highest tensile strength among the six pultruded glass-fiber-reinforced composites. CF/PMMA shows the highest tensile strength apart from CF/epoxy.

Flexural Strength

The pultruded GF/PMMA composites in this study showed the highest flexural strength except for GF/PPS and GF/UP. However, CF/PMMA is some-

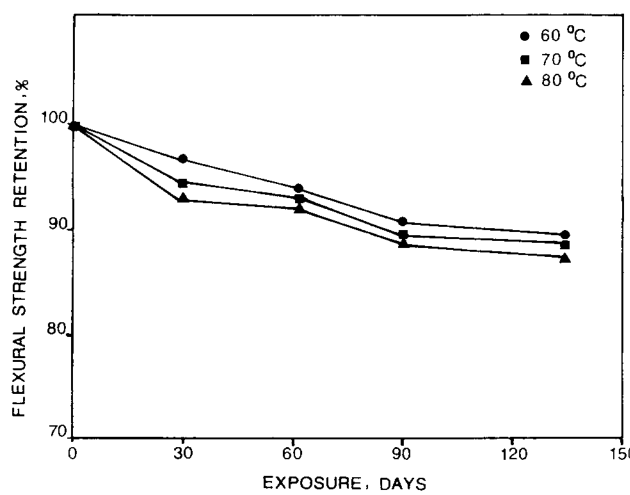

Figure 6 Hygrothermal (85% RH) effect on the flexural strength of pultruded GF/PMMA composites.

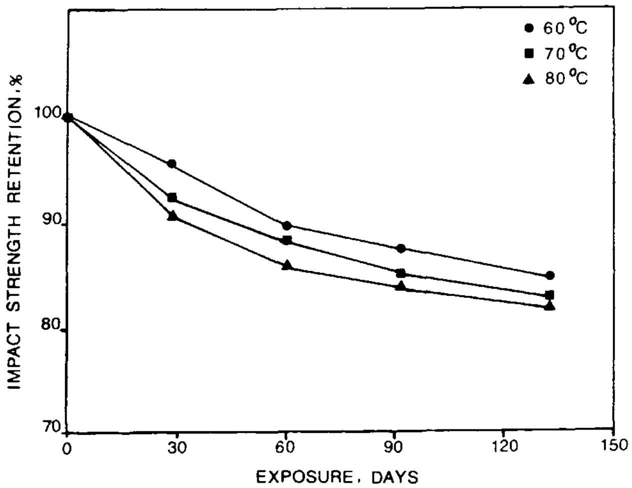

Figure 7 Hygrothermal (85% RH) effect on the notched Izod impact strength of pultruded GF/PMMA composites.

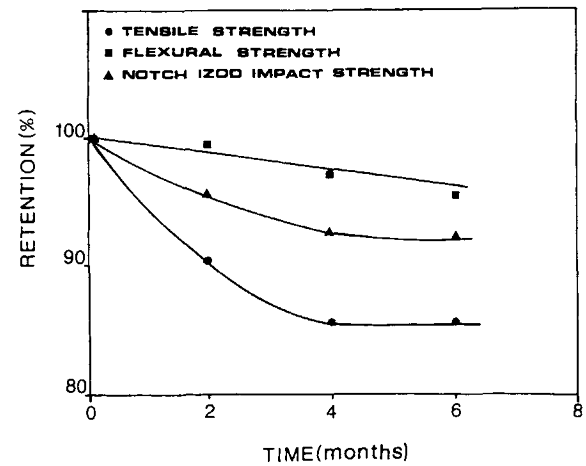

Figure 8 Property retention vs. exposed time of pultruded GF/PMMA composites at RH = 85%, temp = 35°C: (●) tensile strength; (■) flexural strength; (▲) notched Izod impact strength.

what lower in flexural strength among the five pultruded carbon-fiber-reinforced composites.

Heat Deflection Temperature (HDT)

In general, thermoset composites show higher HDT than thermoplastic composites. HDT of pultruded GF/PMMA composites are higher than GF/ABS[22] composites, but lower than GF/NY6, GF/UP, and GF/PH[21] composites. However, CF/PMMA is somewhat lower in HDT among the five pultruded carbon-fiber-reinforced composites.

Dynamic Mechanical Properties

The dynamic shear storage modulus (G') of various pultruded composites are illustrated in Figure 11. One can observe that the dynamic shear storage modulus (G') of the pultruded glass-fiber-reinforced PMMA composites are higher than those of pultruded nylon 6 and polyester composites.[14] At low temperature, one can observe that the dynamic shear storage modulus (G') of pultruded PMMA composites is 10^{10}–10^{11} dyne/cm^2 (typical glassy state). When the temperature is near the glass transition temperature (T_g) 110–130°C, the G' decreases sharply and finally levels off at 10^7–10^8 (typical rubbery state). The decreasing G' indicates that the stiffness of these composites begins to decrease at T_g. However, when the temperature is near T_g, pultruded nylon 6 and polyester composites decreased smoothly due to their being semicrystalline polymers. The PMMA resin, being an amorphous polymer, shows a more abrupt decline in G'.

Effects of the pulling rate on the dynamic mechanical properties (G', G'') of pultruded GF/PMMA composites are shown in Figures 12 and 13. As can be seen in the figures, the dynamic shear storage and loss modulus (G' and G'') increase with decreasing pulling rate, since the conversion of polymer and wetting out of fibers by PMMA resin at low pulling rate were more complete, and the molecular weight increased with decreased pulling rate.

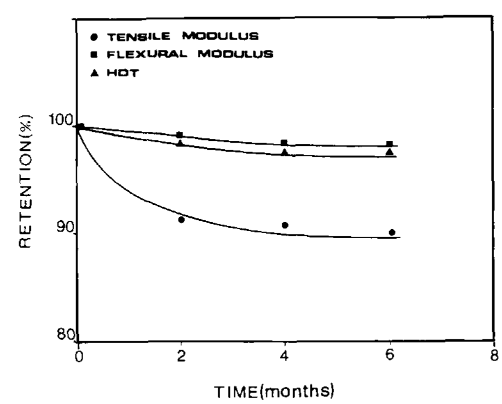

Figure 9 Property retention vs. exposed time of pultruded glass-fiber-reinforced PMMA composites at RH = 85%, temp = 35°C: (●) tensile modulus; (■) flexural modulus; (▲) HDT.

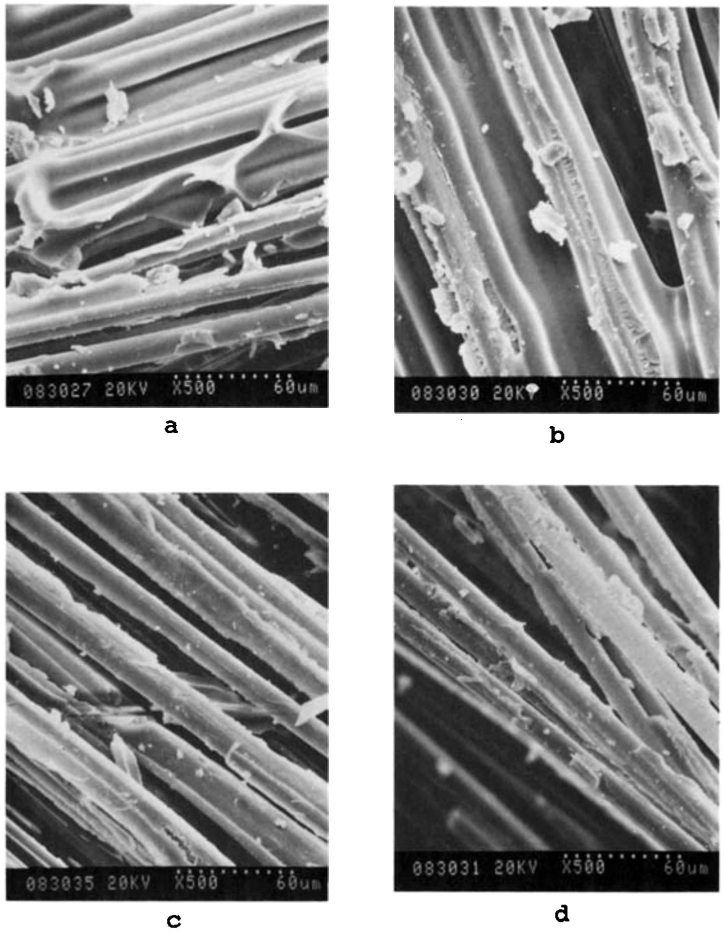

Figure 10 Scanning electron micrograph (SEM) of pultruded glass-fiber-reinforced PMMA composites were exposed to the environment of 85% RH and 35°C: (a) virgin; (b) after 2 months; (c) after 4 months; (d) after 6 months.

CONCLUSIONS

A thermoplastic PMMA resin system was developed for the pultrusion process. In this research, the feasibility of pultrusion processing of glass fiber, carbon fiber, and Kevlar fiber reinforced PMMA composites has been demonstrated.

Mechanical and thermal properties of pultruded PMMA composites increasing with increase fiber volume content. Kevlar 49 fiber/PMMA composites possess the highest specific tensile strength and HDT, while carbon fiber/PMMA composites show the highest tensile strength and tensile modulus. Glass fiber/PMMA composites have the highest specific flexural strength.

Pultruded glass-fiber-reinforced PMMA composites exhibit good weather resistance. The retention of flexural strength and notched Izod impact strength were more than 88 and 82%, respectively, when they are exposed to 85% RH and 60, 70, and 80°C for 135 days. More than 85% of the tensile strength, tensile modulus, and notched Izod impact strength are retained, and more than 95% of the flexural strength, flexural modulus, and HDT are retained when test specimens are exposed to %RH and 35°C for 6 months.

It was demonstrated that the PMMA pultruded products can be postformed or reshaped by thermoforming (at 190°C) under pressure (at 1000 psi) for 10 min. The mechanical properties of postformed products can be improved and show excellent flexural strength and tensile strength compared to other pultruded composites (GF/nylon 6, GF/UP, GF/phenolic, GF/ABS, etc.).

The dynamic mechanical measurement results have shown the dynamic shear storage modulus (G')

Table V Properties Comparison among Pultruded Glass Fiber (GF) Reinforced PMMA, Nylon 6 (NY6), PPS, Unsaturated Polyester (UP), Phenolic (PH), and ABS Resin Composites

Properties	GF/PMMA	GF/NY6	GF/PPS	GF/UP	GF/PH	GF/ABS
Fiber content (wt %)	75	75	72	75	73	75
Tensile strength MPa	848	869	793	828	448	710
(ksi)	(123)	(126)	(115)	(120)	(65)	(103)
Flexural strength MPa	579	469	965	828	483	538
(ksi)	(84)	(68)	(140)	(120)	(70)	(78)
Notched Izod impact kJ/M	2.0	2.4	3.1	2.1	2.1[a]	2.5[a]
(ft-lb/in.)	(38)	(44)	(58)	(40)	(40)	(47)
HDT °C	108	184	> 260	260	> 280	100
(°F)	(226)	(363)	(> 500)	(500)	(> 536)	(212)
References	This study	20	15	15	21	22

[a] Notched Charpy impact strength.

Table VI Properties Comparison among Pultruded Carbon Fiber (CF) Reinforced PMMA, Nylon 6 (NY6), PPS, Phenolic (PH), and Epoxy Resin Composites

	CF/PMMA	CF/NY6	CF/PPS	CF/PH	CF/Epoxy
Fiber content (vol %)	58	57	56	58	54.4
Tensile strength MPa	1503	1496	1172	1103	1917
(ksi)	(218)	(217)	(170)	(160)	(278)
Flexural strength MPa	434	498	1365	827	1213
(ksi)	(63)	(72.3)	(198)	(120)	(176)
Notched Izod impact J/M	1174	1708	1601	2562[a]	2364[a]
(ft-lb/in.)	(22)	(32)	(30)	(48)	(44.3)
HDT °C	118	195	280	280	
(°F)	(245)	(383)	(536)	(536)	
References	This study	20	15	21	4

[a] Notched Charpy impact strength

of the PMMA pultruded composites are higher than those of pultruded nylon 6 and polyester composites. The shear storage modulus of pultruded PMMA composites decreased sharply when the temperature is over T_g, but those of the pultruded nylon 6 and polyester composites decreased smoothly. The dy-

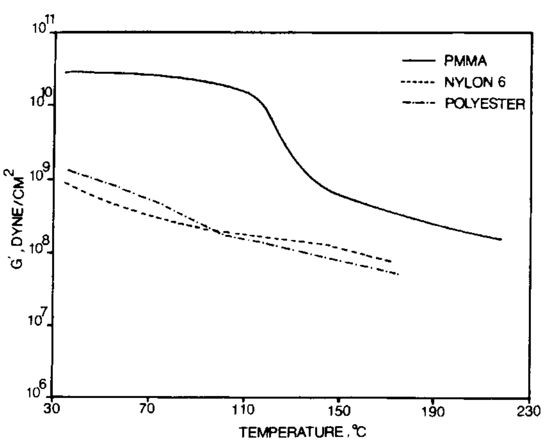

Figure 11 Dynamic shear storage modulus (G') vs. temperature of various pultruded composites: (——) PMMA; (- - -) nylon 6; (- • - •) polyester.

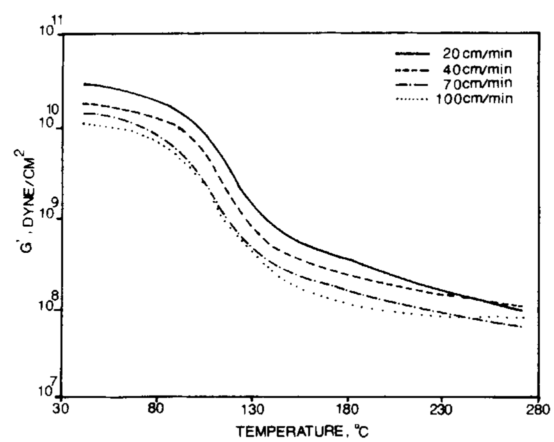

Figure 12 Dynamic shear storage modulus (G') of pultruded GF/PMMA composite at various pulling rates (cm/min): (——) 20; (- - -) 40; (- • - •) 70; (• • •) 100.

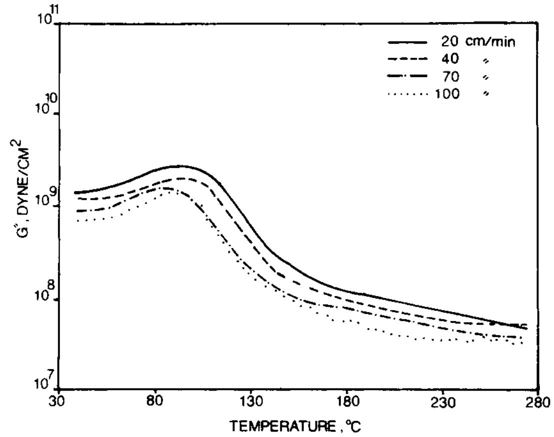

Figure 13 Dynamic shear loss modulus (G'') of pultruded GF/PMMA composite at various pulling rates (cm/min): (——) 20; (- - -) 40; (- • - •) 70; (• • •) 100.

namic storage and loss modulus (G' and G'') of pultruded fiber-reinforced PMMA composites increased with decreasing pulling rate.

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REFERENCES

1. R. W. Meyer, *Handbook of Pultrusion Technology*, Chapman and Hall, New York, 1985.
2. Robert Adolhp Florentine, *37th Annu. Conf., RP/C, SPI*, 10-B (1982).
3. Raymond R. Hindersinn (Pultruded Reinforced Phenolic Resin Products), U.S. Pat. 4,419,400 (1983).
4. J. S. Hwang, Master thesis, National Tsing Hua University, Taiwan, Republic of China, 1986.
5. G. A. Hunter, *43rd Annu. Conf., RP/C, SPI*, 6-C (1988).
6. Y. A. Tajima and D. G. Crozier, *Polym. Eng. Sci.*, **28**, 491 (1988).
7. S. R. Dai and M. R. Piggott, *Polym. Compos.*, **7**, 435 (1986).
8. A. Sternfield, *Mod. Plast.*, (Jan.), 36 (1987).
9. H. Ng and I. Manaszloczower, *Polym. Eng. Sci.*, **29**, 302 (1989).
10. M. L. Wilson, G. S. Johnson, and R. Miserentino, *42nd Annu. Conf., RP/C, SPI*, 1-A (1987).
11. S. G. Hill, E. E. House, and J. T. Hoggatt, Boeing Aerospace Company for Naval Air Systems Command, Contract N00019-77-C0561 (1979).
12. D. E. Beck, *38th Annu. Conf., RP/C, SPI*, 20-C (1983).
13. A. R. Madenjian, N. J. Tessier, and N. R. Schott, *40th Annu. Conf., RP/C, SPI*, 11-F (1985).
14. H. Ishida and G. Rotter, *43rd Annu. Conf., RP/C, SPI*, 6-A (1988).
15. James E. O'Connor, *SAMPE Quart.*, (Apr.), p. 32 (1987).
16. D. E. Beck, *38th Annu. Conf., RP/C, SPI*, 4-D (1985).
17. W. B. Goldsworthy, *Plast. World*, (Aug.), 56 (1984).
18. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Dekker, New York, 1974, p. 483.
19. J. Theberge, J. Crosby, and M. Hutchins, *40th Annu. Conf., RP/C, SPI*, 4-C (1985).
20. C. C. M. Ma and M. S. Yn, Taiwan, R. O. C. Pat. 35,969 (1989).
21. C. C. M. Ma and W. C. Shih, U. S. Pat. 4,873,128 (1989).
22. J. S. Hwang, S. N. Tong, S. J. Hsu, P. H. H. Hsu, and P. T. K. Wu, *43rd Annu. Conf., RP/C, SPI*, 6-E (1988).

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