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Abstract

Aramid-reinforced composite materials of equal fiber volume and varied polymer thermoset matrices were pultruded and flexurally tested to failure. The objective was to improve the flexural properties of aramid-reinforced pultrusions. Pultrusions of both sized and unsized aramid fiber with four different resin systems were compared to determine the effects of sizing compounds and postcuring on flexural strength, fiber wettability, and fiber-to-resin interface bonding. Improvements in flexural strength resulting from pretreatments with the sizing solutions used in this study were marginal. The most significant improvements in flexural properties resulted from postcuring. Flexural strengths ranged from a low of 39 647 psi (273 MPa) to a high of 80 390 psi (554 MPa), an overall increase of 103 percent. The fact that postcuring improved the flexural properties of the pultrusions of the four resin systems indicates that a full cure did not occur in any of the systems during the pultrusion process. The increased flexural strengths of the polyester and vinyl ester pultrusions were the most surprising. Of the four resin systems examined (Co-Rezyn[1] VE 8300 vinyl ester, Aropol[2] 7430 polyester, and Epon[3] 9302 and Epon 9310 epoxies) for aramid-reinforced pultrusion, the highest flexural strength was obtained with Epon 9310 epoxy.

Introduction

The mechanical properties of aramid-reinforced polyester pultrusions have been compared with those of fiberglass-reinforced polyester and vinyl ester pultrusions (ref. 1). The aramid- and fiberglass-reinforced pultrusions contained fiber volumes of 41 percent and 38 percent, respectively. The aramid fiber pultrusion exhibited very poor flexural strength (54 000 psi (372 MPa)) when compared with the strength of fiberglass-reinforced materials (132 000 psi (910 MPa)). The low flexural strength of the aramid pultrusion agrees with the low compressive and flexural values reported by others (refs. 2 and 3). This characteristic is believed to be partially related to the need for some type of pretreatment or sizing compound application to the aramid fibers prior to pultrusion. With this information as background, four resin systems were selected as matrices for aramid-polymer (thermoset) pultrusion experiments. Pultrusions were made with sized and unsized Kevlar 49[4] unidirectional roving (22 720 denier). All materials tested had identical volume fractions of aramid fiber. Three-point flexural tests were conducted and fiber wettability was evaluated. The objective of these experiments was to improve fiber wetting characteristics and fiber-to-matrix interface bonding and thereby increase flexural strength.

This report describes the investigation of the pultrusions of four resin systems with aramid reinforcement fibers, presents test results, and gives an analysis of the results. The authors acknowledge the assistance of Jane M. Hogge and James E. Justice for mechanical testing and Edward W. Covington III for scanning electron microscope (SEM) work and evaluation.

Approach

The pultrusion die used throughout the experiment was 30 in. (76.2 cm) in length, machined from 17-4 PH stainless steel. The die cavity surfaces were polished to 4 microinches (1.02×10^{-7}m) root-mean-square. The die produced pultrusions having cross sections 0.243 in. (0.62 cm) thick and 0.296 in. (0.75 cm) wide. The four resin systems used in the experiment were (1) Aropol 7430 isophthalic polyester, (2) Co-Rezyn VE 8300 vinyl ester, (3) Epon 9302 epoxy, and (4) Epon 9310 epoxy. (See table I.) Both epoxy systems are new experimental epoxy resins of the bisphenol A/ephichlorohydrin type. Unsized aramid fiber roving was unwound, sized, dried, and rewound for use in the program.

Test and Results

The pultruded materials were flexurally tested in the as-pultruded condition and also after various postcuring treatments. Test specimens 3 in. (7.6 cm) in length were used in accordance with the American Society for Testing and Materials (ASTM) Standard D790 (three-point flexural test). This test was used to evaluate improvements in the strength of the pultrusions obtained by varying processing parameters. The failure mode of the specimens was a combination of compression, tension, and shear (ref. 4). The test results are given in table II. The mean strength of five specimens tested in each condition is reported. In the as-pultruded condition, the material with 9310 epoxy matrix exhibited the highest flexural strength; and the material with the polyester 7430 matrix, the lowest. Aramid fiber roving sized with a polyester solution[5] was used with the polyester and 9302 epoxy

[1] Trademark of Interplastic Corporation.

[2] Trademark of Ashland Chemical Company.

[3] Trademark of Shell Chemical Company.

[4] Trademark of E. I. Du Pont de Nemours & Co., Inc.; the generic name for Kevlar is aramid fiber and its chemical name is poly (*P*-phenylene terephthalamide).

[5] Aropol 7430 polyester, 0.5% by weight in acetone.

pultrusions, whereas aramid fiber roving sized with a vinyl ester solution[6] was used with the vinyl ester and 9310 epoxy pultrusions. The changes in flexural strength resulting from sizing applications for the as-pultruded state were (1) an increase of 6.4 percent for polyester, (2) a 17.3-percent decrease for vinyl ester, (3) a 7.6-percent increase for 9302 epoxy, and (4) a 4.3-percent increase for 9310 epoxy. Table II shows that for the aramid-polyester pultrusion, sizing the aramid fibers with a polyester solution increased flexural strength up to postcuring temperatures of 325°F (162°C); however at 400°F (204°C) sizing decreased flexural strength. This suggests that the sizing compound might have begun to degrade. This effect may also explain the reduction caused by sizing in flexural strength of the aramid-epoxy pultrusions above a postcuring temperature of 450°F (232°C). The most significant changes resulted from postcuring. Flexural strengths ranged from a low of 39 647 psi (273 MPa) for unsized polyester in the as-pultruded condition to a high of 80 390 psi (554 MPa) for unsized 9310 epoxy postcured at 450°F (232°C) for 2 hr, an overall increase of 103 percent. The maximum increase in flexural strength of the unsized pultrusions because of postcuring was (1) for the polyester matrix, 87 percent; (2) for the vinyl ester matrix, 50 percent; (3) for the 9302 epoxy matrix, 19 percent; and (4) for the 9310 epoxy matrix, 17 percent. The two conventional pultrusion matrices, polyester and vinyl ester, exhibited the greatest flexural strength increases resulting from postcuring. This was contrary to the expected results (the epoxies were expected to benefit most by postcuring). The 9310 epoxy pultrusion had the highest flexural strength in all conditions.

Figures 1 through 4 are SEM photomicrographs showing the fractured faces of specimens machined from materials with the lowest and highest flexural strengths in each resin system. The polyester resin system (fig. 1(a)) appears to have wetted the aramid fibers least, as indicated by loose and bare fibers, whereas the 9310 epoxy system (fig. 4(b)) appears to have wetted the fibers best of the four resins. The vinyl ester (fig. 2) appears to be second best in wettability. These findings support the quantitative flexural test results listed in table II and graphically compared in figure 5.

Concluding Remarks

Four thermoset resin systems were used as matrices for aramid fiber pultrusions. Fiber volumes were held constant. Pultrusions with both sized and unsized fiber were subjected to varied postcuring temperatures and flexurally tested to failure. Test results are presented to determine the effects of postcuring and sizing pretreatments on the flexural strength of aramid-reinforced pultrusions. The objective was to improve flexural properties by improving fiber wettability and fiber-to-resin interface bonding. Improvements in flexural strength resulting from pretreatments with the sizing solutions used in this study were marginal. More effort needs to be directed toward this approach. The most significant improvements in flexural strength resulted from postcuring. The overall increase was 103 percent. The fact that postcuring improved the flexural properties of the pultrusions indicates that a full cure did not occur in any of the systems during the pultrusion process. The increased flexural strengths of both the polyester and the vinyl ester pultrusions were the most surprising. Of the four resin systems examined for aramid-reinforced pultrusion, the greatest flexural strength was obtained with 9310 epoxy. More tests need to be conducted to determine the thermo-oxidative stability at postcuring temperatures of sizing compounds and resin systems used in pultrusion. In future experiments designed to study wetting characteristics of aramid fibers pultruded in epoxy matrices, very low concentrations of epoxy sizing solutions are recommended to increase fiber wettability. It is also recommended that a tube-type curing oven be installed between the cure die and the pullers to perform the postcuring operation.

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[6] Co-Rezyn VE 8300 vinyl ester, 3% by weight in acetone.

Table I. Resin Systems and Formulations

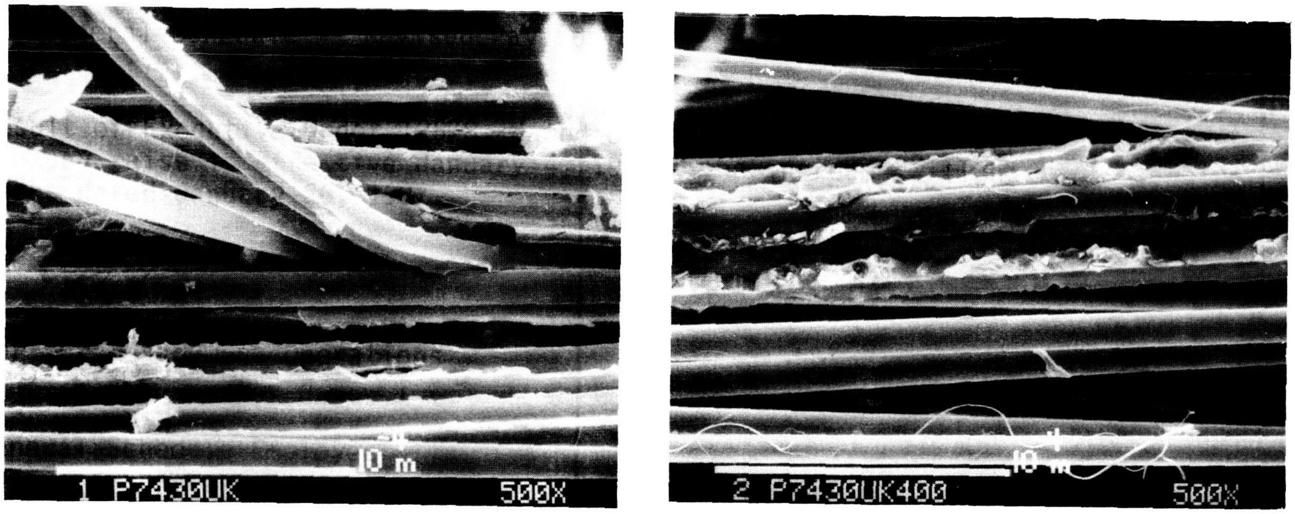
Ashland Aropol 7430 polyester		Interplastic Co-Rezyn VE 8300 vinyl ester		Shell Epon 9302 epoxy		Shell Epon 9310 epoxy	
Constituent	pph	Constituent	pph	Constituent	pph	Constituent	pph
Aropol 7430	100.0	VE 8300	100.0	Epon 9302	100.0	Epon 9310	100.0
ASP 400[a]	10.0	ASP 400	10.0	ASP 400	10.0	ASP 400	10.0
Molgard[b] X	1.0	Molgard X	1.5	Molgard X	2.0	Molgard X	2.0
Microthene FS500[c]	.8	P16N[d]	.6	CA 9350[e]	3.0	CA9360[f]	32.5
P16N	.5	TBPB[g]	.4			BGE[h]	8.1
TBPB	.3						
Viscosity, cP	800	Viscosity, cP	630	Viscosity, cP	780	Viscosity, cP	570
Cure temp., °F	300	Cure temp., °F	315	Cure temp., °F	400	Cure temp., °F	400

[a]Alumina silicate powder (filler).
[b]Internal release agent; trademark of Ram Chemicals Div., Whittaker Corp.
[c]Internal release agent; trademark of U.S. Industrial Chemicals Co.
[d]Percadox 16N (catalyst); trademark of Noury Chemical Corp.
[e]Epon curing agent 9350; trademark of Shell Chemical Co.
[f]Epon curing agent 9360; trademark of Shell Chemical Co.
[g]Tertiary-butyl perbenzoate (catalyst).
[h]Butyl glycidyl ether.

Table II. Ultimate Flexural Strength for Aramid-Reinforced Pultrusions

[All test specimens contained fiber volume fraction 0.46; fiber orientation was unidirectional. All tests were conducted at room temperature]

Condition		Ultimate flexural strength, psi, for—			
Sizing	Postcure	7430 polyester	VE 8300 vinyl ester	9302 epoxy	9310 epoxy
Unsized	As pultruded	39 647	50 045	57 372	68 554
Sized	As pultruded	42 192	41 376	61 751	71 474
Unsized	285°F, 2 hr	65 312	67 662	67 121	74 230
Sized	285°F, 2 hr	68 009	69 377	59 115	72 749
Unsized	325°F, 1 hr	68 322	70 935	67 488	75 273
Sized	325°F, 1 hr	68 489	69 974	66 780	75 214
Unsized	400°F, 2 hr	74 361	75 088	62 164	77 335
Sized	400°F, 2 hr	70 430	78 844	68 298	79 452
Unsized	450°F, 2 hr			62 344	80 390
Sized	450°F, 2 hr			68 053	76 550
Unsized	500°F, 35 min			68 061	80 014
Sized	500°F, 35 min			65 278	77 108



(a) Unsized aramid fiber; as pultruded; 39 647 psi flexural strength.

(b) Unsized aramid fiber; 400°F postcure; 74 361 psi flexural strength.

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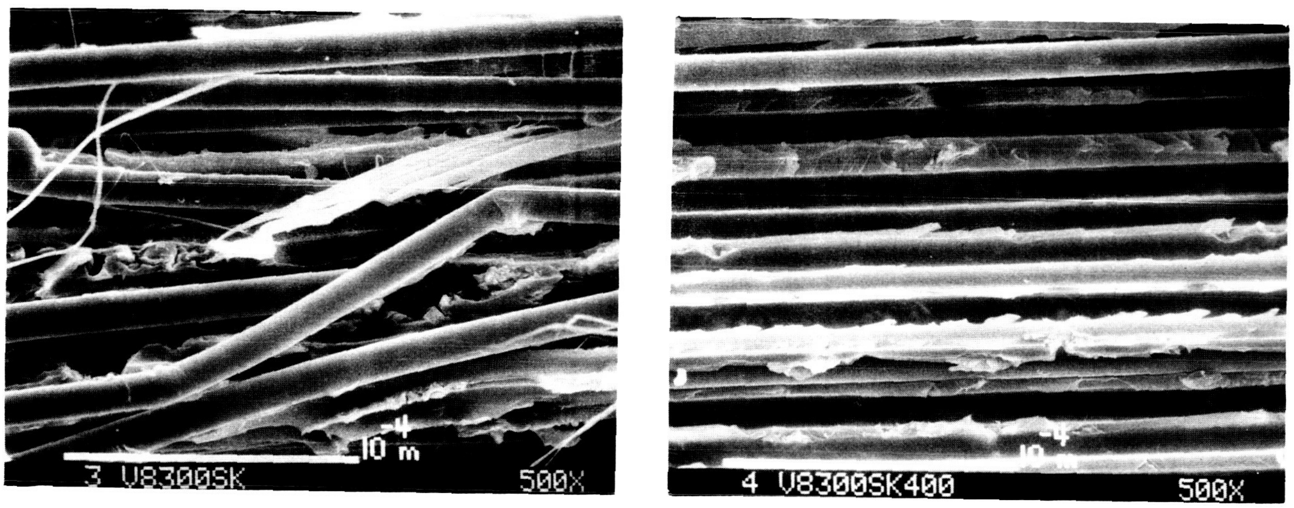
Figure 1. Fracture face SEM photomicrographs of aramid-polyester 7430.

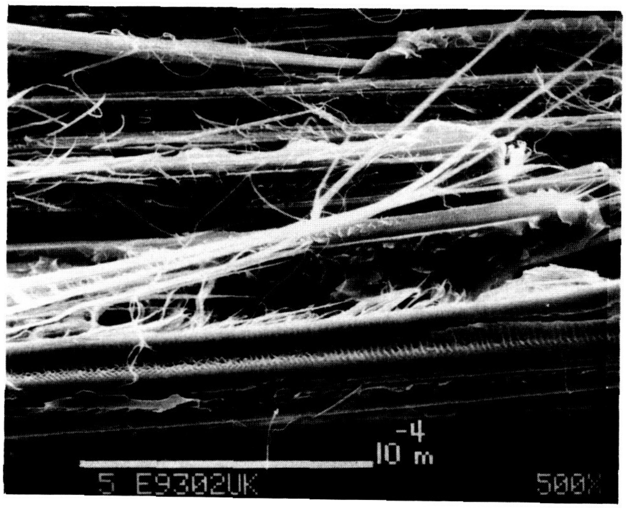


(a) Sized aramid fiber; as pultruded; 41 376 psi flexural strength.

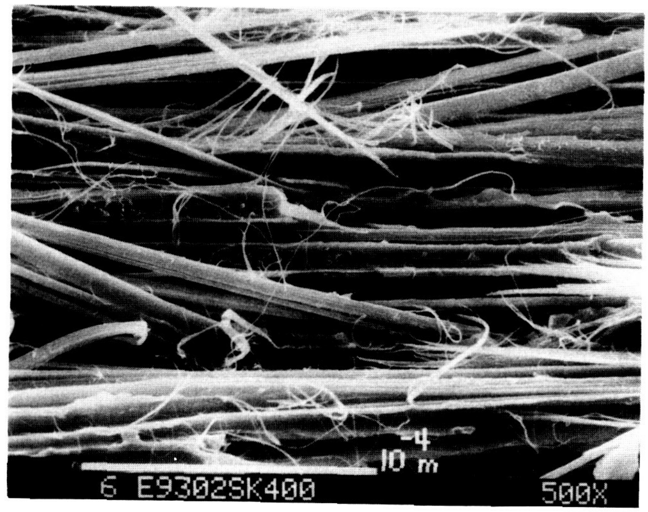
(b) Sized aramid fiber; 400°F postcure; 78 844 psi flexural strength.

L-86-405

Figure 2. Fracture face SEM photomicrographs of aramid-vinyl ester 8300.



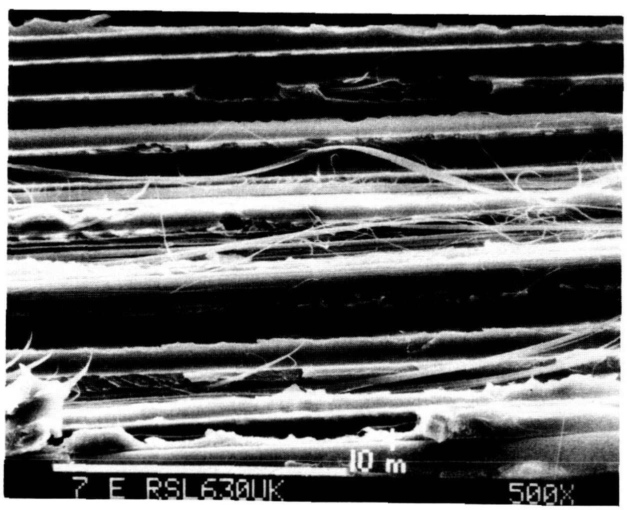
(a) Unsized aramid fiber; as pultruded;
57 372 psi flexural strength.



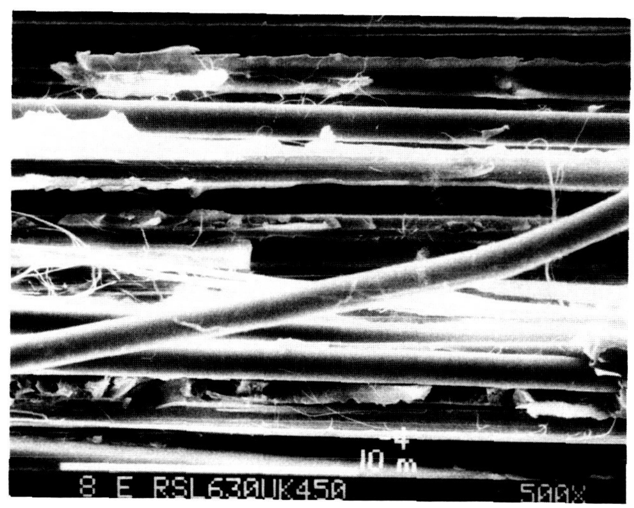
(b) Sized aramid fiber; 400°F postcure;
68 298 psi flexural strength.

L-86-406

Figure 3. Fracture face SEM photomicrographs of aramid-epoxy 9302.



(a) Unsized aramid fiber; as pultruded;
68 554 psi flexural strength.



(b) Unsized aramid fiber; 450°F postcure;
80 390 psi flexural strength.

L-86-407

Figure 4. Fracture face SEM photomicrographs of aramid-epoxy 9310.

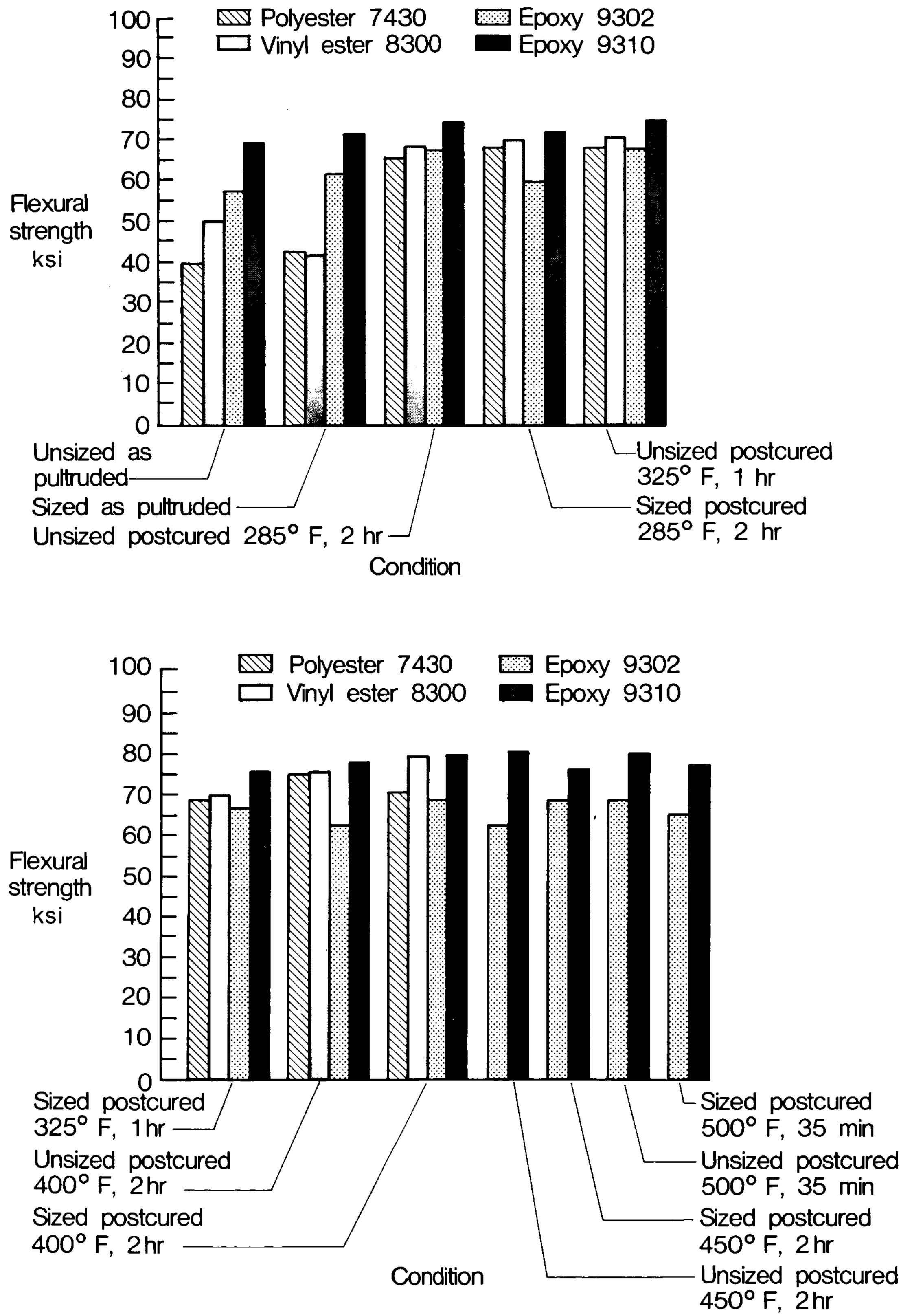


Figure 5. Flexural strengths of 46 percent aramid fiber pultrusions.

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15. Supplementary Notes

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Aramid-reinforced composite materials of equal fiber volume and varied polymer thermoset matrices were pultruded and flexurally tested to failure. The objective was to improve the flexural properties of aramid-reinforced pultrusions. Pultrusions of both sized and unsized aramid fiber with four different resin systems were compared to determine the effects of sizing compounds and postcuring on flexural strength, fiber wettability, and fiber-to-resin interface bonding. Improvements in flexural strength resulting from pretreatments with the sizing solutions used in this study were marginal. The most significant improvements in flexural properties resulted from postcuring. Flexural strengths ranged from a low of 39 647 psi (273 MPa) to a high of 80 390 psi (554 MPa), an overall increase of 103 percent. The fact that postcuring improved the flexural properties of the pultrusions of the four resin systems indicates that a full cure did not occur in any of the resin systems during the pultrusion process. The increased flexural strengths of the polyester and vinyl ester pultrusions were the most surprising. The four resin systems examined were Interplastic Corporation VE 8300 vinyl ester, Ashland Chemical Company Aropol 7430 Polyester, and Shell Chemical Company Epon 9302 and Epon 9310 epoxies.

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