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FIBER-MATRIX INTERFACE STUDIES ON ELECTRON BEAM CURED COMPOSITES

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ABSTRACT

The recently completed Department of Energy (DOE) and industry sponsored Cooperative Research and Development Agreement (CRADA) entitled, "Electron Beam Curing of Polymer Matrix Composites," determined that the interlaminar shear strength properties of the best electron beam cured IM7/epoxy composites were 19 - 28% lower than autoclave cured IM7/epoxy composites (ie. IM7/977-2 and IM7/977-3). Low interlaminar shear strength is widely acknowledged as the key barrier to the successful acceptance and implementation of electron beam cured composites in the aircraft/aerospace industry. The objective of this work was to improve the interlaminar shear strength properties of electron beam cured composites by formulating and evaluating several different fiber sizings or coating materials. The researchers have recently achieved some promising results by having discovered that the application of epoxy-based, electron beam compatible sizings or coatings onto surface-treated, unsized IM7 carbon fibers improved the composite interlaminar shear strength properties by as much as 55% versus composites fabricated from surface-treated, unsized IM7 fibers. In addition, by applying these same epoxy-based sizings or coatings onto surface-treated, unsized IM7 fibers it was possible to achieve an 11% increase in the composite interlaminar shear strength compared to composites made from surface-treated, GP-sized IM7 fibers. Work is continuing in this area of research to further improve these properties.

KEY WORDS: Electron Beam Curing, Epoxy, Fiber Sizings

1. INTRODUCTION

In 1994 the Department of Energy (DOE) sponsored a Cooperative Research and Development Agreement (CRADA) involving the Oak Ridge National Laboratory

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DISCLAIMER

(ORNL), the Oak Ridge Y-12 Plant, Sandia National Laboratory, and 10 industrial companies entitled "Electron Beam Curing of Polymer Matrix Composites" (1). This CRADA led to a better understanding and utilization of electron beam curing technology for processing polymer matrix composite materials and it resulted in the development of new electron beam curable cationic epoxy resin systems possessing many favorable composite properties (2-4). Many of these properties are equivalent to or better than those of autoclave cured composites, except for the interlaminar shear strength properties which are about 19 - 28% lower than those of autoclave cured composites (ie. IM7/977-2 and IM7/977-3). Table 1 compares the various IM7 laminate properties of electron beam cured versus autoclave cured composites.

Low interlaminar shear strength is widely acknowledged as the key barrier to the successful acceptance and implementation of electron beam cured composites in the aircraft/aerospace industry. Several researchers involved in the curing of composites via electron beam have thought that the interlaminar shear properties could be improved by using carbon fiber sizings which are more compatible with electron beam curable cationic epoxy resin systems. The carbon fiber sizings that are currently in use today have been engineered and optimized over the last several decades specifically for use in thermal curing of composites, not electron beam curing. The objective of this work was to initiate a first step approach towards improving the interlaminar shear strength properties of electron beam cured composites by formulating and evaluating several electron beam compatible fiber sizings or coating materials. This preliminary effort was not designed to completely solve the interface problem, but it was intended to provide valuable information in support of a new CRADA project that is focused specifically on resolving this issue. This new CRADA effort entitled, "Interfacial Properties of Electron Beam Cured Composites," is slated to begin in the spring of 1999.

2. EXPERIMENTAL

2.1 Materials and Processes The epoxy resins used for formulating the fiber sizings/coatings were obtained from Shell Chemical Company and Dow Chemical Company. These are described below:

Shell Epon 826: Liquid diglycidyl ether of bisphenol A resin having a viscosity of 6,000-9,500 cps at room temperature and a weight per epoxide of 178-186.

Shell Epon Resin 1001F: Solid diglycidyl ether of bisphenol A resin having a melting point of 79°C and a weight per epoxide of 525-550.

Shell Epon Resin 1007F: Solid diglycidyl ether of bisphenol A resin having a melting point of 125°C and a weight per epoxide of 1,700-2,300.

Dow D.E.N. 439: Solid epoxy novolac resin having a softening point of 48° - 58°C and a weight per epoxide of 191-210.

Cationic initiator: The cationic initiator, Sarcat SR-1012, used in formulating the sizings/coatings and rendering them electron beam curable was purchased from the Sartomer Company.

Carbon Fibers: IM7-12K GP-sized and IM7-12K unsized carbon fibers were purchased from the Hexcel Corporation and Adherent Technologies Incorporated.

Carbon fiber coating trials: All carbon fiber coating trials were conducted at Adherent Technologies, Inc. in Albuquerque, New Mexico and were performed using their fiber coating line and tube furnace under the direction of Dr. Ronald Allred.

Filament winding resin: The electron beam curable filament winding resin was formulated using Union Carbide's ERL-2258 and 3 parts of initiator per hundred parts of resin (phr) of (4-Octyloxyphenyl)phenyliodonium hexafluoroantimonate (OPPI). The OPPI was purchased from General Electric as Product UV9392C.

Electron Accelerator: All electron beam irradiation work was graciously provided by Acsion Industries, Inc. Pinawa, Manitoba, Canada, under the direction of Mr. Vincent Lopata using the Atomic Energy of Canada, Ltd. (AECL) I-10/1 Electron Linear Accelerator (Energy: 10 MeV; Power: 1 kW).

2.2 IM7 Fiber Coating Trials The formulated fiber sizings/coatings (Table 2) were applied onto surface treated, unsized IM7 carbon fibers by first unspooling the carbon fiber tow from the fiber package using a tensioned roller, immersing the fibers into a solvent (acetone or methyl ethyl ketone) bath containing the coating resin, evaporating the solvent from the fiber tow by passing them through a heated tube furnace, then respooling the fiber onto a cardboard tube. Several concentrations of epoxy resins with or without cationic initiator were evaluated in our trials. The epoxy resin concentrations in acetone or MEK ranged from about 1 - 10% and the cationic initiator concentration, relative to the epoxy, ranged from about 1 - 3 phr. The speed that the fiber was traveling during the coating and drying process was 9.1 or 10.7 meters per minute (30 or 35 feet per minute) while the temperature of the drying tube furnace ranged from 165° - 200°C. Depending upon the coating concentration, the type of formulation that was used, and the speed at which the fiber was traveling, the final weight content of the dried fiber coatings on the IM7 fibers ranged from 0.2 - 10%.

2.3 Filament Winding The coated carbon fibers were then used for filament hoop winding a series of 15.24 cm (6 in) inner diameter, 0.3175 cm (0.125 in) thick, 10.16-12.7 cm (4-5 in) wide composite cylinders onto aluminum mandrels. The electron beam curable resin used for fabricating the filament wound cylinders was ERL-2258 with 3 phr OPPI initiator. In addition to the above cylinders, two control cylinders were also produced, including one using commercially available, surface-treated, and unsized IM7 carbon fiber, and one fabricated using commercially available, surface-treated, and GP-sized IM7 carbon fiber. The justification for using the GP-sized fiber as the control in this work versus using other commercially available fibers stemmed from the fact that over the last several years a large amount of mechanical property data has been generated on electron beam cured composites made with the GP-sized IM7 fiber. The filament winding resin used to fabricate both control cylinders was ERL-2258 with 3 phr OPPI initiator. Filament winding of all of the cylinders was conducted at room temperature.

2.4 Electron Beam Curing and Specimen Preparation After the cylinders were fabricated they were placed in individual saddles of a plywood box and shipped to Acsion Industries in Pinawa, Manitoba, Canada, where they were electron beam cured using a pulsed, 10 MeV, 1 kW electron beam linear accelerator. The cylinders were cured in 9 passes at about 17 kGy per pass for a total dose of approximately 150 kGy. During the electron beam curing cycle the cylinders were individually rotated and remotely conveyed fore and aft with the length of the mandrel positioned perpendicular to the length of the scan horn. After cure the cylinders were shipped back to Oak Ridge and machined along the fiber direction into 1.90 cm (0.75 in) long x 0.635 cm (0.25 in) wide short-beam-shear specimens and tested in interlaminar shear per ASTM D2344.

3. RESULTS

Table 2 details the specific IM7 fiber sizings/coating formulations: process parameters for coating, filament winding, and electron beam curing; and the results on the composite interlaminar shear strength (ILSS) values. Eighteen specimens (six specimens from three different locations) were tested per cylinder for obtaining an average ILSS. The ILSS data comparing the surface-treated, unsized specimens (EB2F) versus the surface-treated, GP-sized specimens (EB4A) versus the surface-treated-coated composite specimens (EB4D) averaged 60, 84, and 93 MPa (8708, 12118, and 13457 psi), respectively. For the EB4D (Epon 1001F with 3 phr CD1012) coated composite specimens, these values translate into a 55% improvement in ILSS relative to the surface-treated, unsized specimens (EB2F), and an 11% improvement in ILSS relative to the surface-treated, conventional GP-sized specimens (EB4A). This improvement is very encouraging since the epoxy coatings which were used to coat the IM7 carbon fibers were applied to surface-treated, unsized fibers which were several months old. It is thought that unsized carbon fibers which are several months old have lost some percentage of their original surface functionality and are therefore not as likely to bond to the matrix resin as well as those fibers that are sized/coated immediately after the fiber surface treatment process. On future work this assumption will be further evaluated to determine whether it is possible to improve the ILSS beyond the level of these early, but very promising results. Figures 1 and 2 are scanning electron micrographs (SEM) of surface-treated and unsized IM7 carbon fibers that were previously coated out of an acetone solution containing about 10% by weight Epon 1001F epoxy resin and dried in the tube furnace.

A key finding is that these epoxy coating formulations can improve composite ILSS. The vast majority of epoxy coating formulations that were applied onto the aged, surface-treated, and unsized IM7 fibers yielded composites that had ILSS properties significantly greater than those of composites made with the aged, surface-treated, and unsized (control) fiber. This positive finding supports the argument for further developing sizing or coating strategies that can potentially improve the fiber-matrix interphase properties and adhesion.

In Figure 3 there does not appear to be a relationship between the epoxy concentration of a given epoxy coating resin with no initiator, in this case Epon 1001F, and its effect on the ILSS of electron beam cured composites. In Figures 4-6 the maximum ILSS for the lower melting and lower weight per epoxide Epon 1001F coatings is improved by using a greater amount of initiator (3 phr versus 1 phr) and a lower epoxy coating concentration (1% versus 6%). On the other hand, for coating compositions involving the higher melting and higher weight per epoxide Epon 1007F formulations, or the higher melting, epoxy novolac DEN 439 materials, or the low viscosity, difunctional epoxy Epon 826 formulations, the trends for optimizing the ILSS are favored by using lesser amounts of initiator or no initiator (0 phr or 1 phr versus 3 phr) in combination with lower epoxy concentrations (1% versus 6%).

4. CONCLUSIONS

We have demonstrated that by applying epoxy-based, electron beam compatible sizings or coatings onto surface-treated, unsized IM7 carbon fibers one can improve the composite interlaminar shear strength properties by as much as 55% versus composites fabricated from surface-treated, unsized IM7 fibers. In addition, by applying these same epoxy-based sizings or coatings onto surface-treated, unsized IM7 fibers we have shown an 11% increase in the composite interlaminar shear strength properties compared to composites made from surface treated, GP-sized IM7 fibers. Additional work in this area is currently

being conducted since it is anticipated that the interlaminar properties can be further improved beyond the levels discussed in this effort.

5. ACKNOWLEDGEMENTS

The authors would like to thank Mr. Vincent Lopata of Acsion Industries, Inc. Pinawa, Manitoba, Canada, who graciously provided all of the electron beam irradiation support.

6. REFERENCES

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Table 1. IM7 Laminate Properties (Data Norm. to 62% F.V.) Electron Beam Cured vs. Autoclave Cured

Resin Systems	Fiberite 977-2 (Fiberite Data)	Fiberite 977-3 (Fiberite Data)	Cytec 5250-4 BMI (Cytec Data)	*Electron Beam Resin 8H*	*Electron Beam Resin 10H*	*Electron Beam Resin 9H*	*Electron Beam Resin 3K*	*Electron Beam Resin 1K*	*Electron Beam Resin 1L*
Cure Conditions	Autoclave Cured (6 h @ 177°C [350°F] @ 85 psi)	Autoclave Cured (3 h @ 180°C [355°F] @ 85 psi)	Autoclave Cured (up to 20 h @ 232°C [450°F] @ 85 psi)	*250 kGy (Sec.-Min. @ RT @ Vacuum Bag Press. Only)*	*150 kGy (Sec.-Min. @ RT @ Vacuum Bag Press. Only)*	*150 kGy (Sec.-Min. @ RT @ Vacuum Bag Press. Only)*	*150 kGy (Sec.-Min. @ RT @ Vacuum Bag Press. Only)*	*150 kGy (Sec.-Min. @ RT @ Vacuum Bag Press. Only)*	*150 kGy (Sec.-Min. @ RT @ Vacuum Bag Press. Only)*
Void Volume, %	Not Reported	Not Reported	Not Reported	*1.77*	*0.72*	*1.24*	*0.64*	*1.18*	*1.70*
Tg, °C (Tan Delta)	200	190/240	300	*396*	*392*	*232*	*212*	*212*	*237/400*
O° Tens. Str., MPa (ksi)	2537 (368)	2510 (364)	2423 (352)	*1869 (271)*			*2200 (319) Within 9%*		*2262 (328) Within 7%*
O° Tens. Mod., GPa (msi)	166 (24.1)	162 (23.5)	150 (21.7)	*168 (24.3)*			*157 (22.8)*		*164 (23.8)*
82° (180°F) Hot/Wet O° Tens. Str., MPa (ksi)	2362*** (343)			*2282** (331)*			*2365** (343)*		*2386** (346)*
82°C (180°F) Hot/Wet O° Tens. Mod., GPa (msi)	167*** (24.3)			*172** (24.9)*			*177** (25.7)*		*166** (24)*
O° Flex. Str., MPa (ksi)	1641 (238)	1765 (256)	1594 (231)	*1986 (288)*	*2006 (291)*	*1793 (260)*	*1765 (256)*	*1710 (248)*	
O° Flex. Mod., GPa (msi)	147 (21.3)	150 (21.7)	144 (21)	*196 (28.5)*	*163 (23.6)*	*163 (23.7)*	*154 (22.3)*	*150 (21.8)*	
O° Comp. Str., MPa (ksi)	1580 (230)	1682 (244)	1499 (217)	*1683 (244)*			*1428 (207)*		*1524 (221)*
O° Comp., Mod., GPa (msi)	152 (22)	154 (22.3)	146 (21.3)	*149 (21.6)*					
82°C (180°F) Hot/Wet O° Comp. Str., MPa (ksi)	1240*** (180)			*1407** (204)*			*1324** (192)*		*1386** (201)*
O° ILSS, MPa (ksi)	110 (16)	127 (18.5)	139 (20.2)	*77 (11.2) Within 30%*	*79 (11.5) Within 28%*	*79 (11.5) Within 28%*	*89 (12.9) Within 19%*	*77 (11.2) Within 30%*	
Hot/Wet O° ILSS*, MPa (ksi)	72 (10.4)	89 (12.9)		*61 (8.8) Within 32%*					
H_2 Perm., Kp (Perm. Rate Constant, Uncycled @ RT & -196°C [-320°F]) scc mm/atm sec cm^2				*9.22×10^{-9} & $<2.97 \times 10^{-9}$*			*3.43×10^{-8} & 1.62×10^{-8}*		*1.03×10^{-8} & $<4.90 \times 10^{-9}$*
* 1 wk. in H_2O @ 71°C (160°F), 977-3 & Electron Beam 8H tested @ -104°C (220°F) (977-2 tested @ 82°C [180°F])	** 4 days in H_2O @ 82°C (180°F)	*** 7 days in H_2O @ 74°C (165°F)	Electron beam comps. prepared using conv. lay-up methods. Int. debulks @ vacuum/4plies @ RT, 15 min. Final debulk @ vacuum, 70°C, 1 h.						

Table 2. Effects of Epoxy Coated Carbon Fibers on the Interlaminar Shear Strength of Electron Beam Cured, Filament Wound Cylinders.

Carbon Fiber (IM7-12K) Epoxy Coating Trials				Results		
Sample ID	Sizing	Epoxy Coating Material	Soln. Conc. (Phr Epoxy in Acetone or MEK)	ASTM D 2344 Short Beam Shear Strength (MPa)	ASTM D 2344 Short Beam Shear Strength (psi)	% Coefficient of Variation (Std. Dev./Avg., n=18)
EB2A	Unsized	Epon 1001F	1	69	9991	4.00
EB2B	Unsized	Epon 1001F	2.25	72	10428	2.90
EB2C	Unsized	Epon 1001F	3.5	68	9886	4.70
EB2D	Unsized	Epon 1001F	6	67	9764	4.00
EB2E	Unsized	Epon 1001F	10	77	11169	4.90
EB4C	Unsized	Epon 1001F w/ 1 phr CD1012	1	74	10784	6.00
EB4D	Unsized	Epon 1001F w/ 3 phr CD1012	1	93	13457	4.00
EB4E	Unsized	Epon 1001F w/ 1 phr CD1012	6	78	11288	3.10
EB4F	Unsized	Epon 1001F w/ 3 phr CD1012	6	78	11305	2.00
EB4B	Unsized	Epon 1007F	1	71	10244	2.80
EB1E	Unsized	Epon 1007F	6	71	10320	3.10
EB1D	Unsized	Epon 1007F w/ 1 phr CD1012	1	72	10377	4.60
EB1F	Unsized	Epon 1007F w/ 1 phr CD1012	6	60	8721	2.50
EB3A	Unsized	Epon 1007F w/ 3 phr CD1012	6	56	8098	2.00
EB1A	Unsized	DEN 439	1	76	11016	11.90
EB1B	Unsized	DEN 439	6	66	9625	4.80
EB1C	Unsized	DEN 439 w/ 3 phr CD1012	6	64	9285	5.60
EB3B	Unsized	Epon 826	1	75	10834	4.00
EB3E	Unsized	Epon 826	6	70	10165	5.80
EB3C	Unsized	Epon 826 w/ 1 phr CD1012	1	78	11242	3.20
EB3D	Unsized	Epon 826 w/ 3 phr CD1012	1	69	10015	4.10
EB3F	Unsized	Epon 826 w/ 3 phr CD1012	6	67	9677	2.60
EB2F	Unsized	None	NA	60	8708	4.80
EB4A	Sized	GP-Sized by Vendor	NA	84	12118	3.50

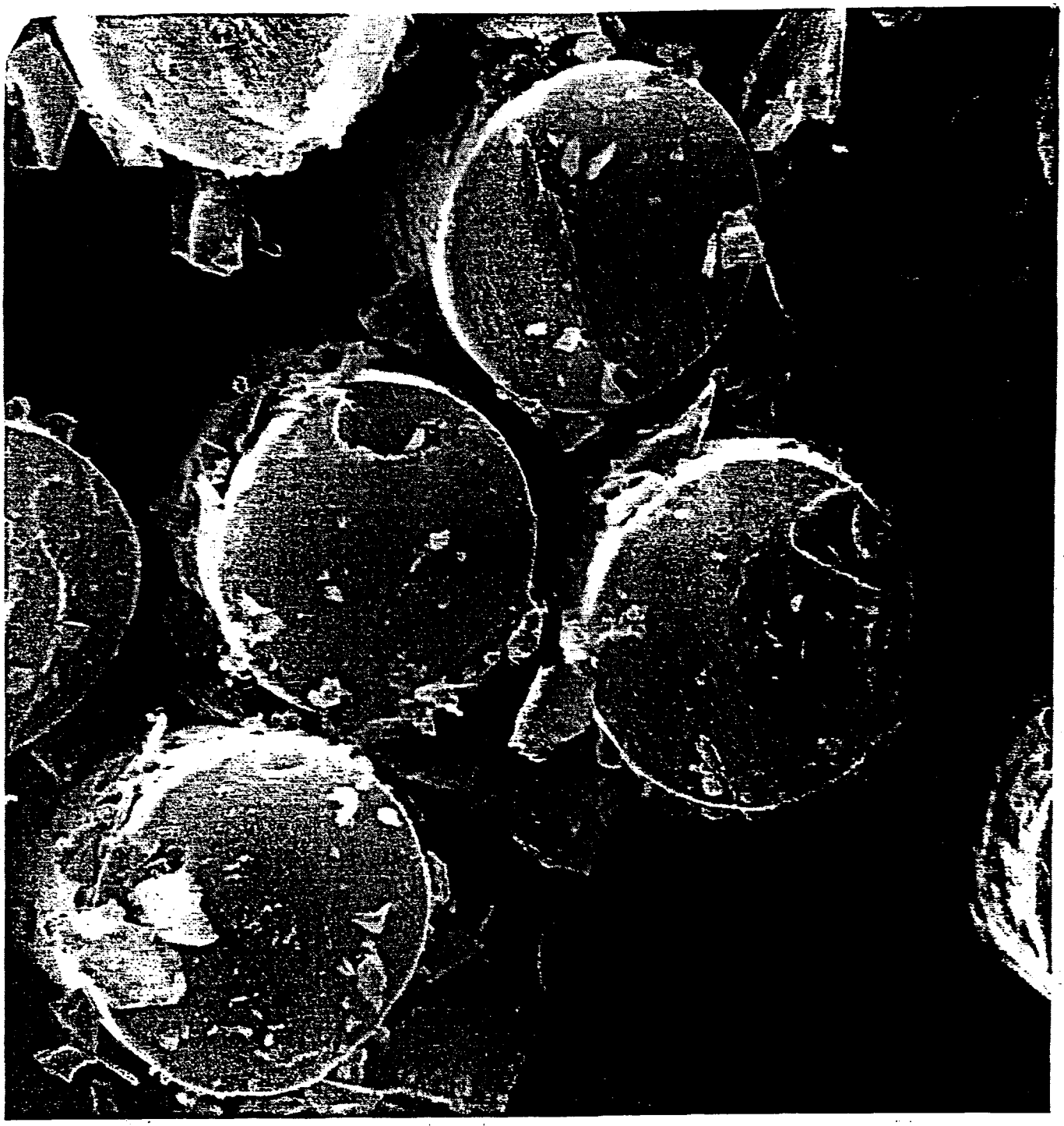

Figure 1. SEM of epoxy coated IM7 Carbon Fibers (6000X). The coating was applied onto the fiber out of a 10% Epon 1001F solution.

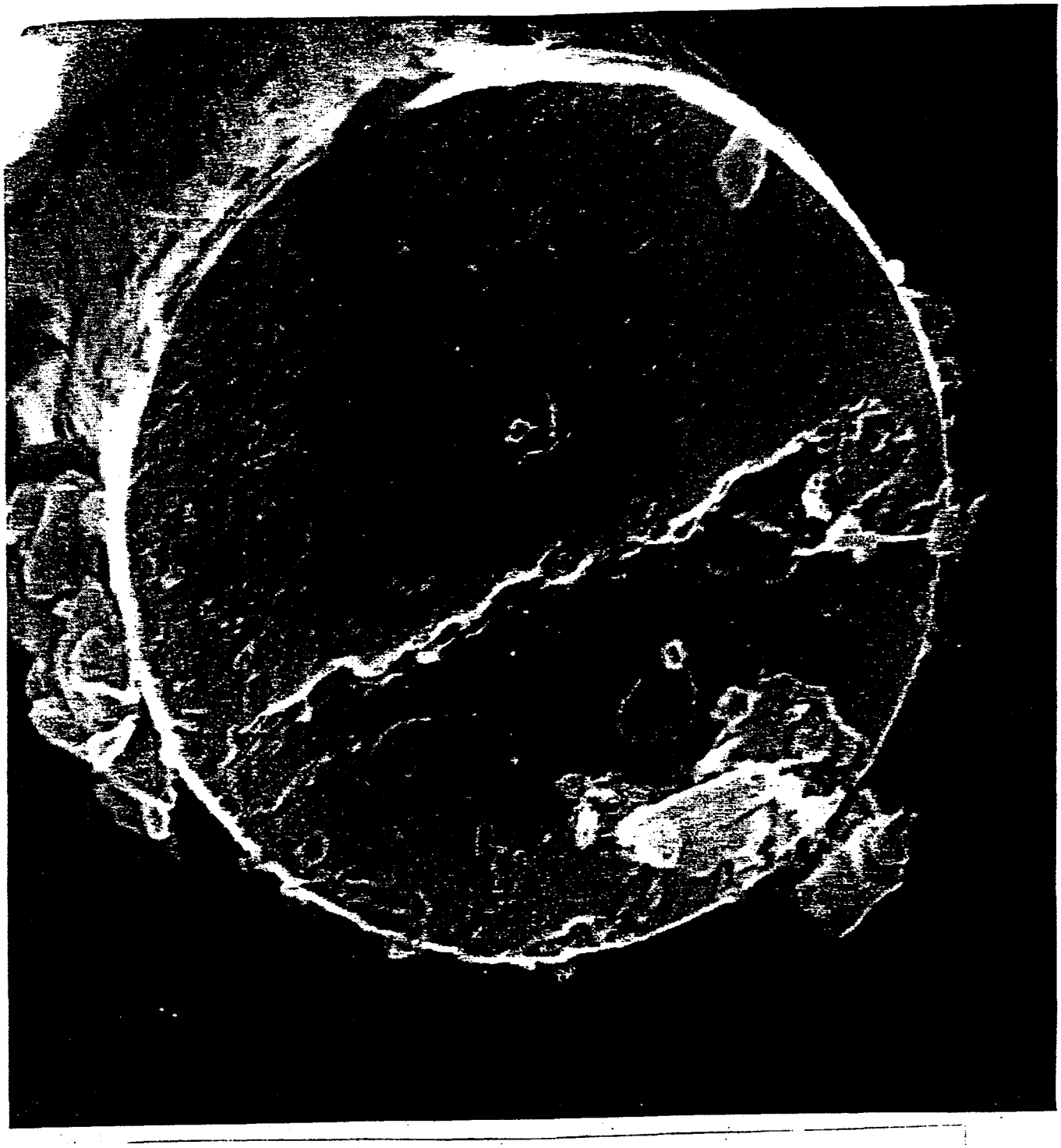

Figure 2. SEM of epoxy coated IM7 Carbon Fiber (15,000K).

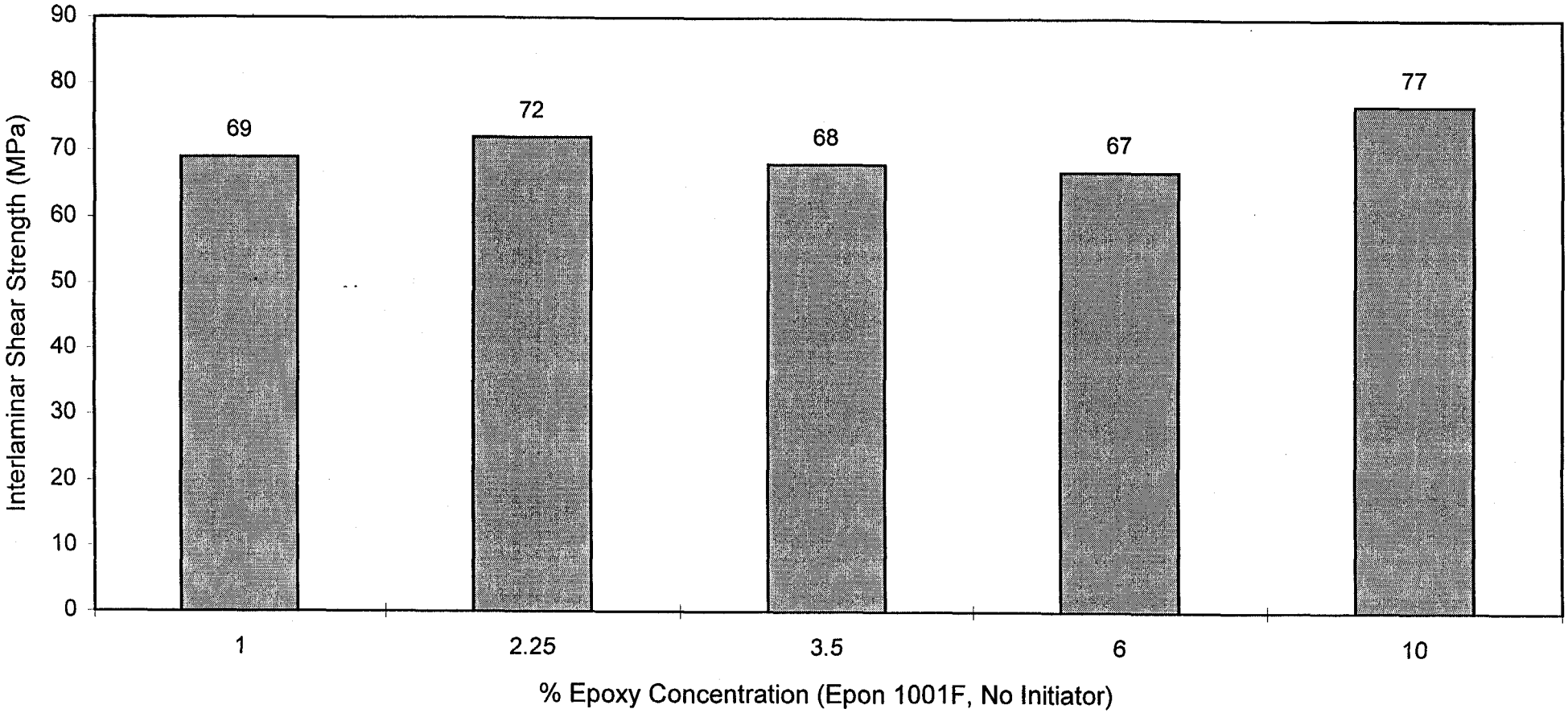

Figure 3. Effect of Epoxy Coating Concentration on the Interlaminar Shear Strength of Electron Beam Cured, Filament Wound IM7 Composite.

Note: The epoxy coatings were applied onto conventionally surface-treated and unsized IM7 fibers out of an epoxy solution. Subsequent to solvent evaporation the fiber was filament wound at RT using ERL 2258/3phr OPPI and electron beam cured at 150 kGy.

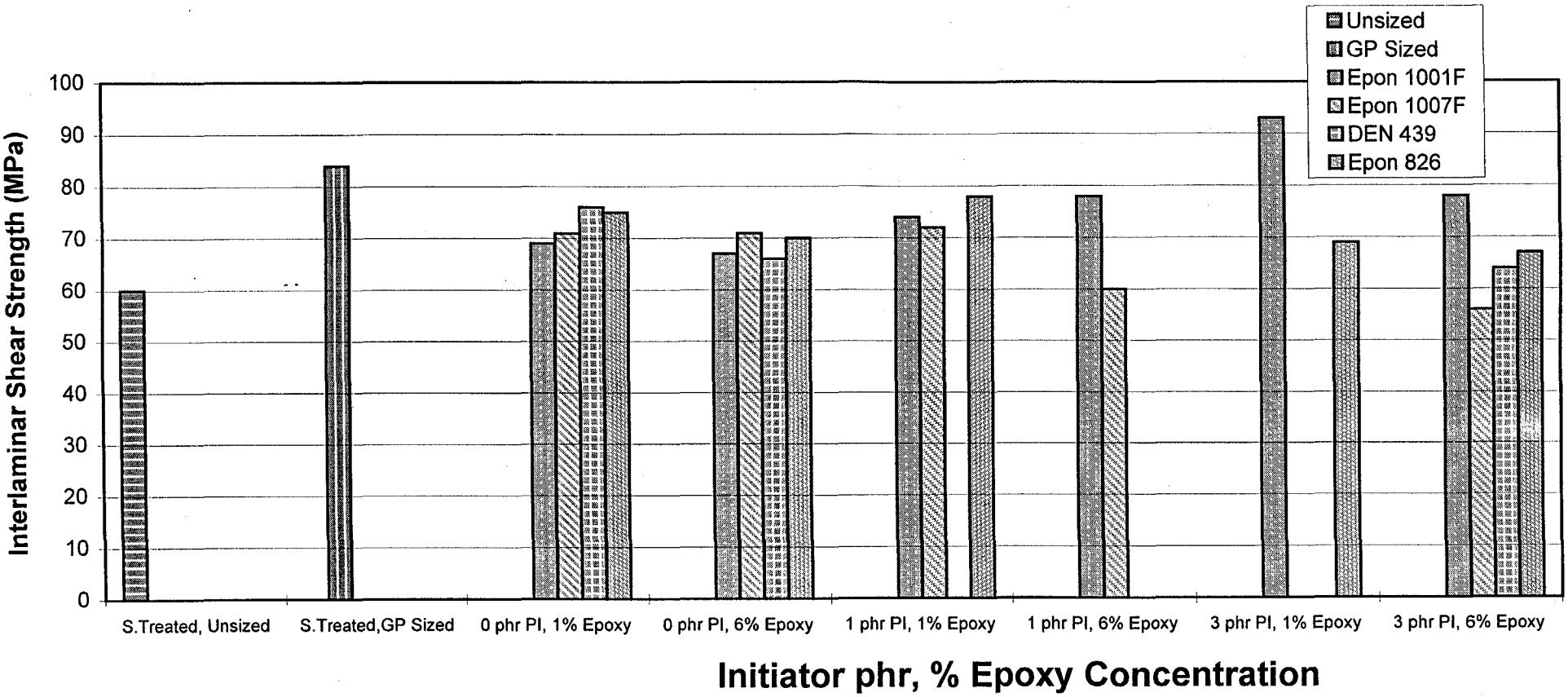

Figure 4. Effects of Epoxy Coating Formulation on the Interlaminar Shear Strength of Electron Beam Cured, Filament Wound IM7 Composites.

Note: On all but the first 2 columns (Controls) the epoxy coatings were applied to surface-treated, unsized fibers out of an epoxy/solvent solution. After solvent evaporation, the fiber was filament wound at RT w/ ERL 2258/3 phr OPPI and electron beam cured at 150 kGy.

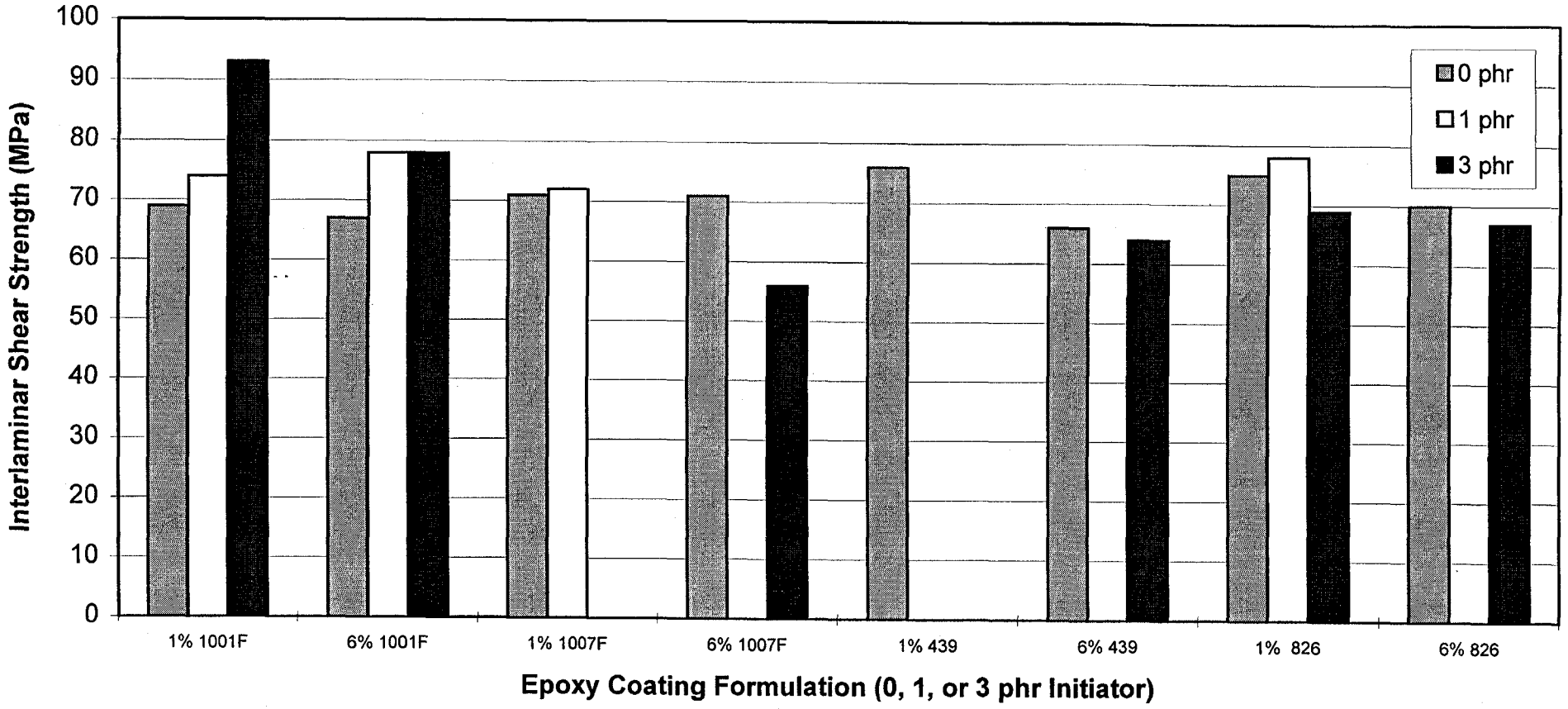

Figure 5. Effects of Epoxy Coating Formulation on the Interlaminar Shear Strength of Electron Beam Cured, Filament Wound IM7 Composite.

Note: The epoxy coatings were applied onto conventionally surface-treated and unsized IM7 fibers out of an epoxy/solvent solution. Subsequent to solvent evaporation, the fiber was filament wound at RT using ERL 2258/3 phr OPPI and electron beam cured at 150 kGy.

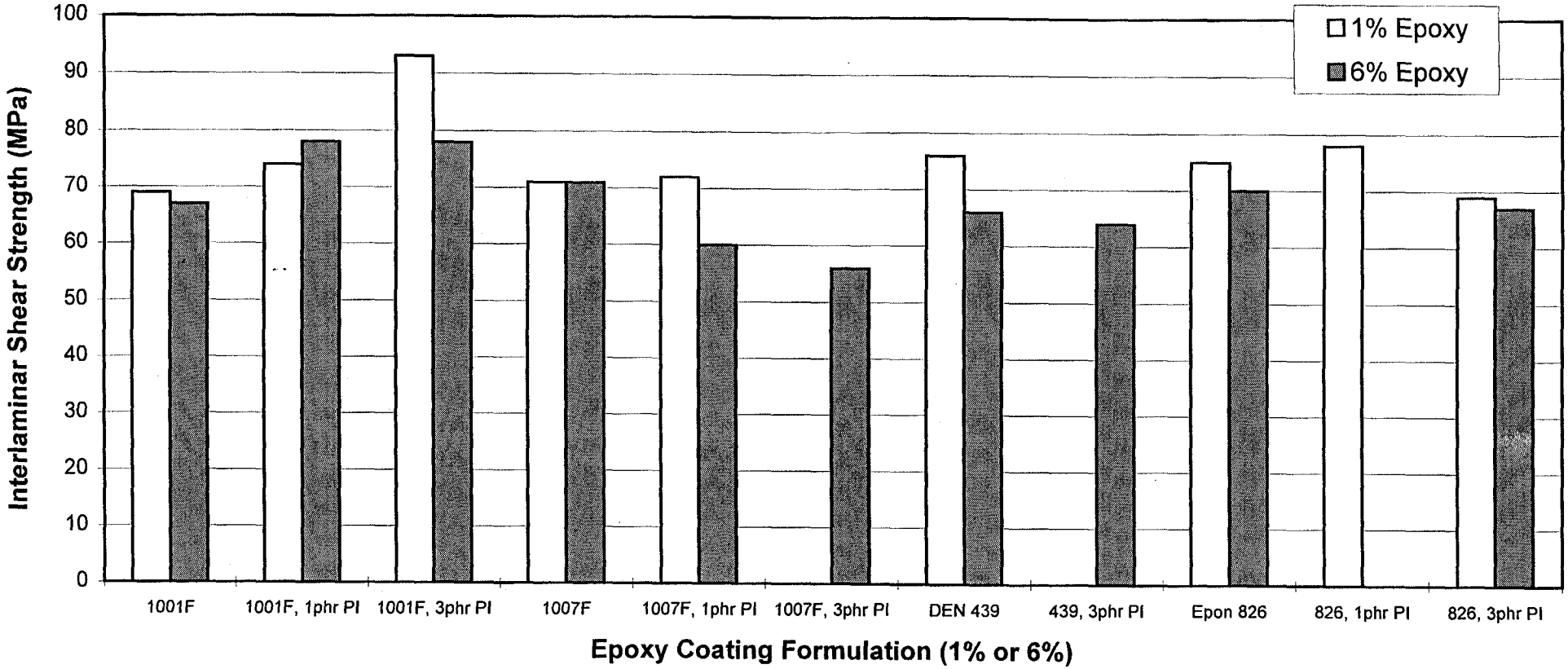

Figure 6. Effects of Epoxy Coating Formulation on the Interlaminar Shear Strength of Electron Beam Cured, Filament Wound IM7 Composite.

Note: The epoxy coatings were applied onto conventionally surface-treated and unsized IM7 fibers out of an epoxy/solvent solution. Subsequent to solvent evaporation, the fiber was filament wound at RT using ERL 2258/3 phr OPPI and electron beam cured at 150 kGy.