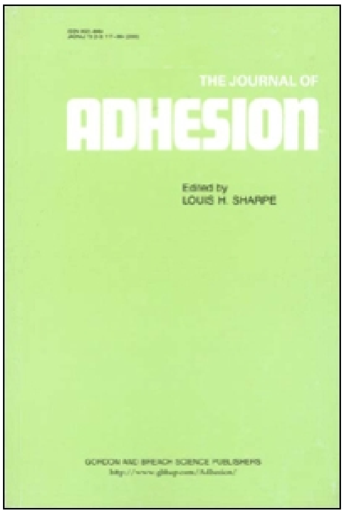

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Interfacial Aspects of Polymer Coating by Electropolymerization[†]

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Polymer coatings were produced on graphite fiber electrodes by electroinitiated polymerization in an electrolytic cell containing monomer. The adhesion of the coated graphite fibers to an epoxy matrix has been measured by single fiber pull-out tests. The measured values of the pull-out force, and scanning electron micrographs of pulled-out fibers reveal three modes of failure and degrees of adhesion independent of the type of polymer coating. It is seen that the initial formation of a resin cone on the embedded fiber contributes significantly to the measured values of the pull-out force for fine, 5–10 μm carbon fibers but not for larger diameter ($>50\ \mu$m) fibers. The effect of the surface treatment on the interfacial properties of composites prepared from the coated fibers was manifested in variations of the interlaminar shear and impact strengths of epoxy composite specimens which were sensitive to the type of coating polymer. Polymer coating of carbon fibers by electrodic processes is thus seen as a promising approach to the study of the polymer interphase in carbon fiber reinforced composites.

1. INTRODUCTION

Comprehensive documentation of studies on electropolymerization of vinyl and other monomers in solution is available presently in a number of reviews.[1–3] The objective of a current investigation in our laboratory is to explore the use of electropolymerization to coat carbon fiber electrode surfaces with polymers formed *in situ*.[4, 5] This process complements electropolymerization in solution and differs from conventional electrocoating processes involving electrophoretic migration and deposition of polymer species carrying ionic charges. We present here results of this study pertaining to the effect

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on fiber–matrix adhesion of polymer coatings formed by electropolymerization on carbon fibers used as electrodes. The manifestation of this effect has been followed by single-fiber pull-out tests and by measurements of interlaminar shear strength of composites prepared from the coated fibers. The variable effects of monomers and solvents used in electropolymerization have also been studied and found to be significant.

Single fiber pull-out techniques which were successful for glass fibers[6, 7] have been unsuccessful for the smaller diameter (5–10 μm) carbon fibers[8] since the thickness of the resin (i.e., the length of the embedded fiber) was too large. A more recent technique which is capable of producing resin buttons as thin as 0.05 mm has been reported[9] but the adhesive strength values obtained varied considerably. The "button" technique has therefore been refined here to measure the adhesive strength of carbon fibers which have been coated with polymer.

2. EXPERIMENTAL

Carbon fibers used as electrodes were placed in the center compartment of a 3-compartment cell, containing solvent, electrolyte, and monomer. Platinum electrodes were placed on each of the two end compartments along with solvent and electrolyte. Electropolymerizations were conducted at constant d.c. voltage.

Specimens for fiber pull-out tests were prepared in which the carbon fiber was held in position along the center of a 7 mm (OD) glass tube by being threaded through a tiny hole in the center of a piece of adhesive tape covering one end of the tube. The hole surrounding the fiber was sealed by a drop of hot sealing wax and mercury was added in. The epoxy resin (100:20/diglycidyl ether of bisphenol A:butyl glycidyl ether with triethylenetetramine (12.8 phr) was added to cover the top of the mercury and thereby enclose the fiber. Curing was conducted at room temperature for at least 3 days. The menisci of the mercury surface and the added resin result in a strong resin button that is extremely thin at the center.[9] Buttons as thin as 14.3 μm have been prepared using this technique. Fibers were pulled from the resin at a speed of 0.008 cm/min using an in-house tensile tester built according to specifications reported in the literature.[10, 11] The diameter of the fibers was measured with a Vickers split image eye piece mounted on a microscope. Fiber lengths were measured with the same instrument from the fiber end to a distinct resin cone which appeared on most of the fibers as seen in scanning electron micrographs. On fibers which adhered very weakly to resin a less pronounced but nonetheless distinguishable collar marked the point at which the fiber entered the resin. The area of contact over which fiber pull-out occurred and the force required for fiber pull-out were calculated from these measurements. Results reported here are for pull-out tests conducted with Hercules AU fibers coated by electropolymerization.

Electropolymerization on graphite fibers which were to be used in composite specimens was conducted as follows. Hercules® AU fiber tow was wound ten times around H-type frames cut from Masonite coated with baked-on epoxy for solvent resistance. Electropolymerization was conducted by positioning this frame in the middle compartment of a Lucite® electropolymerization cell separated by cellulose filter paper. After polymerization, the frame was removed, rinsed and dried in vacuum at 50°C for 12 hours, leaving the coated fibers wound and aligned on the frame.

Prepregs were then prepared by brushing on a DGEBA epoxy resin (EPON® 828) mixture catalyzed by m-phenylenediamine and heating the fibers at 80°±5°C for 1 hour, turning over the frame every 15 minutes to obtain even wetting. After cooling, the impregnated fibers were cut from the frames and trimmed to obtain prepreg tapes approximately 60×178 mm from each frame. Strips 12.7 mm wide were cut from the prepregs with a razor blade parallel to fiber alignment and used in compression molding at 150°C and 200 psi for 30 minutes. Composite bars 12.7 mm wide and approximately 178 mm long were thus obtained, and specimens for the interlaminar shear tests were cut from these pieces.

ASTM standard methods were adopted to measure density (D792–66, A–1), void content (D2734–70, B) and fiber content (D3171–73, B). The measured void content of the specimens was 0.2% maximum. Interlaminar shear tests were conducted according to ASTM D2344–72 on an Instron Tensile Testing machine, Model TTCML, using a center loading flexure fixture, Instron model 1000. Flat-beam specimens 6.4±0.1 mm wide, 25±1.0 mm long and of varying thickness between 4.0 and 5.5 mm were tested at a crosshead speed of 1.0 mm/min, using a span to thickness ratio of 4 to 1. The fiber orientation in the specimen was parallel to its length. The arithmetic average of shear strengths and standard deviations (small sample) of five specimens were reported for each composite. For each electropolymerization system, the interlaminar shear strength was measured at three different fiber volume fractions between 45 and 75%. Most of the specimens failed in shear; and only the values observed for shear failure were adopted. The best straight line through the plots of the shear strength against fiber volume percent was drawn to approximate the shear strength over the 45 to 75% fiber volume range.

3. RESULTS AND DISCUSSION

A. Electropolymerization

It was found that carbon fiber is a good substrate for electropolymerization. As reported in detail elsewhere,[4, 5] polymer coatings were formed from a variety of monomer–solvent–electrolyte systems on several commercially available carbon fibers (Thornel®, Fortafil® and Hercules®) used as electrodes. Polymer presence was observed by weight increases of the fibers after polymerization, scanning electron micrographs, and, when possible, infrared spectral analysis of polymer extracted from the fibers.

The crucial step in forming these polymer coatings was the selection of a solvent–electrolyte system capable of forming a solution of the monomer with sufficient current conducting properties. Dimethyl formamide and dimethyl sulfoxide proved most useful in this respect among organic solvents. Monomers containing a variety of functional groups, terminal vinyl, carboxylic acid, anhydride, epoxy, and aziridinyl, formed polymer coatings by homo- and copolymerizations in aqueous and nonaqueous solvent systems. Employing the techniques of characterization described in the section on experimental methods, a number of interesting and significant observations were made regarding the interfacial aspects of these coatings.

Comparing water and nonaqueous solvents, it appeared that better polymer coatings were produced from aqueous systems. It might be expected that the organic monomers would be adsorbed on and wet the electrode surface better from aqueous systems because of the higher surface tension of water. In nonaqueous systems containing organic solvents of low surface tension, adsorption of the monomer is apparently not well favored and the coatings are consequently inferior. The observations were confirmed by the peeling of coatings formed from different solvent media on metal electrodes over a very much larger surface area. The results emphasize the importance of monomer adsorption to subsequent adhesion of polymer to the electrode.

It was also significant that in many, though not all, monomer systems, the polymer coating was grafted to the carbon fiber electrode.[5] The graphite fibers, coated by electropolymerization, were subjected to continuous solvent extraction for 120 hours to ensure removal of all unbonded polymer which would be soluble. Observed weight increases due to residual polymer and scanning electron micrographs of the extracted fibers confirmed the presence of unextractable polymer. Only in the case of monomers such as methyl methacrylate which normally yield linear soluble polymers, was the retention of insoluble polymer on the fiber surface taken as evidence for grafting. Thus one could conclude that diacetone acrylamide, methyl methacrylate and styrene did form graft polymers by electropolymerization on graphite fibers.

B. Fiber pull-out tests

The plots of force for fiber pull-out from an epoxy matrix against area of contact of carbon fibers coated by electropolymerization of various monomers are presented in Figure 1. The strength of adhesion was calculated from the slopes of these lines. Regardless of the polymer coating, only three values of carbon fiber adhesion to the epoxy resin seem to be present: (a) a weak adhesion (9.7×10^6 N/m^2), (b) a strong adhesion (28.7×10^6 N/m^2), and (c) a *single* intermediate adhesion (18.3×10^6 N/m^2).

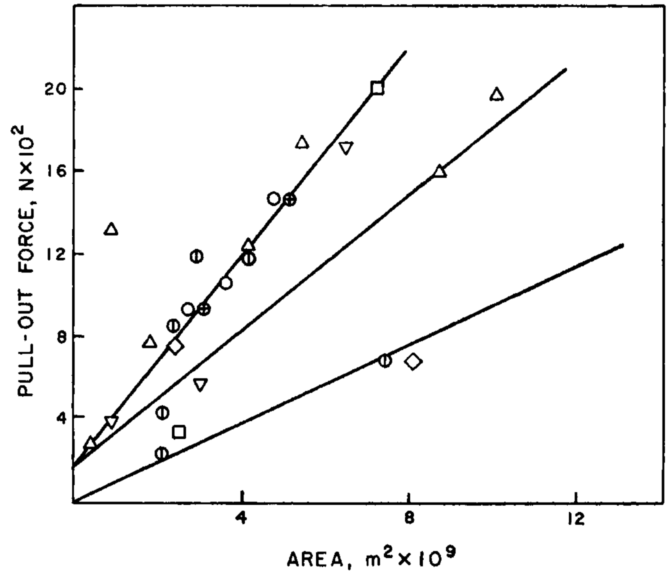

FIGURE 1 Fiber pull-out force versus area of contact with an epoxy matrix for graphite fibers electrocoated with methyl methacrylate (□), diacetoneacrylamide (⦶), styrene (△), styrene-co-acrylonitrile (▽), acrylic acid (⊕), and ε-caprolactam (◇). Untreated fiber (○).

Fibers which adhere strongly have a distinctive collar as seen in Figure 2a, and have much adhering resin. This seems to indicate a failure of the resin pastille, although the value of 28.7×10^6 N/m^2 does not agree with the cohesive strength of the resin itself—48×10^6 N/m^2, determined under about the same conditions as for fiber pull-out. It is not easy to explain the smaller pull-out energy as a cohesive failure. (Larger pull-out energies could be rationalized on the basis of a pull-out area larger than the area of the fiber itself.) Fibers which have an intermediate adhesion have a collar like those indicated in the SEM photograph of Figure 2b. The pulled-out fibers are clean, indicating a fiber-coating failure (Figure 2c). Fibers which have low adhesion have a small but distinctive collar. In addition, the fibers appear to be evenly covered with fluid immediately after being pulled out. After several minutes, this even covering changed in appearance to one such as is shown in SEM photograph Figure 2d. These particularly revealing photographs show the pulled out fiber coated with nonadhering resin. The 9.7×10^6 N/m^2 is

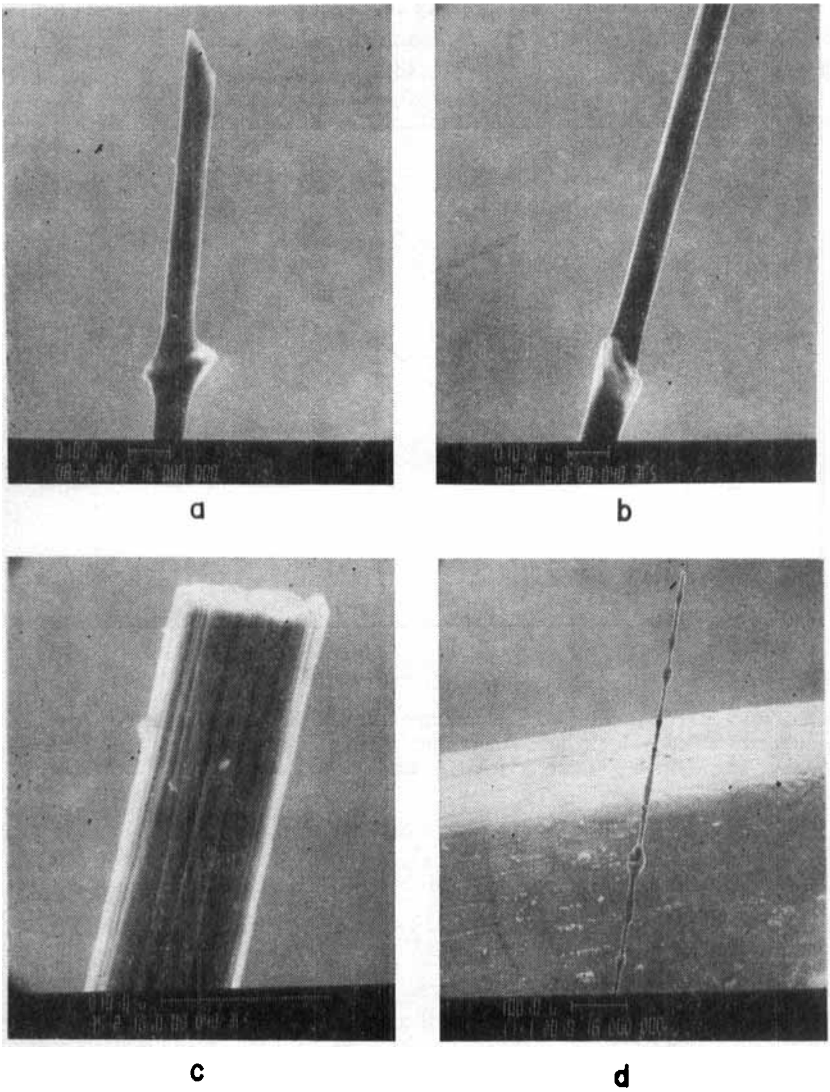

FIGURE 2 Typical SEM pictures of graphite fibers pulled-out from an epoxy matrix corresponding to (a) strong adhesion, (b, c) intermediate adhesion, and (d) weak adhesion curves in Figure 1.

apparently the frictional force of pull-out between the coating and the matrix resin.

The precision of these points and the corresponding linearity of the force, versus embedded area plots gave a result which pointed out a significant source of error not considered in previous carbon fiber adhesion tests. Other investigators calculated the strength of adhesion according to the relationship $\sigma = F/\pi dl$ where F is the pull-out force and d and l the diameter and length of the fiber, respectively. Our results indicate that a plot of F *vs.* πdl does not pass through the origin and that the true relationship is $\sigma = F/\pi dl + C$ where C represents the force required to fracture the resin to produce the resin cone.

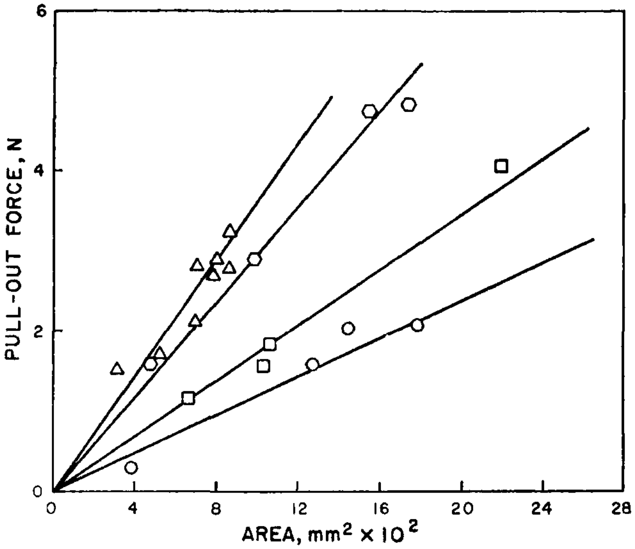

FIGURE 3 Pull-out force versus area of contact with an epoxy matrix of E-glass and basalt fibers; untreated: glass (○), basalt (□); A-1100 silane treated: glass (○) and basalt (△).

The value of C was determined to be 2.0×10^{-2} N. The magnitude of this value indicated that an error of at least 10% and most probably about 25% is present in values for C fiber adhesion which do not consider cone formation. (Because of the much larger pull-out values associated with larger diameter fiber such as glass, the energy required for cone formation does not seem to represent a significant error in their case. This is clearly demonstrated by the set of curves obtained for fiber pull-out from an epoxy matrix of untreated and silane treated E-glass fibers (Figure 3). Also included in this figure are results obtained with basalt fibers, a new mineral fiber produced in our laboratories from basaltic rocks of the Pacific North-west Region.[12] The fiber diameters varied around 100 μm; the silane used was γ-aminopropyl trimethoxy silane (A-1100). The plots easily extrapolate to the origin, and also reflect the improvement in fiber–matrix adhesion caused by silane treatment of the fibers.

In summary, strongly adhering carbon fibers appear to fail at least in part in the matrix. Weakly adhering fibers appear to be coated with a lubricating film. The fibers which have an intermediate adhesion are a mystery. One would initially think that all intermediary values would be possible, yet only one was found for several different samples. Furthermore, most of the pulled-out fibers are clean indicating a coating-fiber interfacial separation. This is also confusing since one would expect that different coatings would adhere differently. In terms of the interfacial interactions between fiber, coating and matrix, the following may approximate the truth in these results.

Strong adhesion:	fiber-coating	good interaction
	coating-matrix	good interaction
Intermediate adhesion:	fiber-coating	fair interaction
	coating-matrix	good interaction
Weak adhesion:	fiber-coating	fair interaction
	coating-matrix	poor interaction

A good interaction between both fiber-coating and coating-matrix interfaces results in failure at the weakest point—often, but not always, in the epoxy matrix itself. The net result is a strongly adhering fiber. When the interaction between the fiber and coating is consistently less than the interaction between coating and matrix, pull-out results in a "clean" fiber and the adhesive strength is "intermediate". Since only one such value occurs it may represent the frictional force of pull-out between fiber and coating. If the interaction between the fiber and coating is only slightly greater than that between coating and matrix, slippage may occur at both interfaces, but the net result is seen to be a coating-matrix failure.

C. Interlaminar shear strength

While the single fiber pull-out tests seemed to be nonspecific with respect to the nature of the polymer coating on the carbon fibers, the interlaminar shear strengths of epoxy matrix composites prepared from the coated fibers yielded much more definitive results. The interlaminar shear strength is taken as a measure of the fiber-matrix adhesion in a composite and this is seen to be altered significantly by the type of polymer coating formed by electropolymerization on the carbon fibers prior to their incorporation in the epoxy matrix.[4, 5] In plots of the shear strength against fiber volume fraction, both increases as well as decreases compared to that of an untreated fiber are observed, thus establishing the manifestation of the effect of interphase modification by electropolymerization. Illustrative results are given in Table 1 and Figure 4. Details can be found in Ref. 5. The time of polymerization, the solvent medium and post-polymerization annealing treatment were additional parameters that influenced the measured shear strength. As discussed earlier, the use of water as solvent appears to be superior to organic solvent systems in improving shear strength.

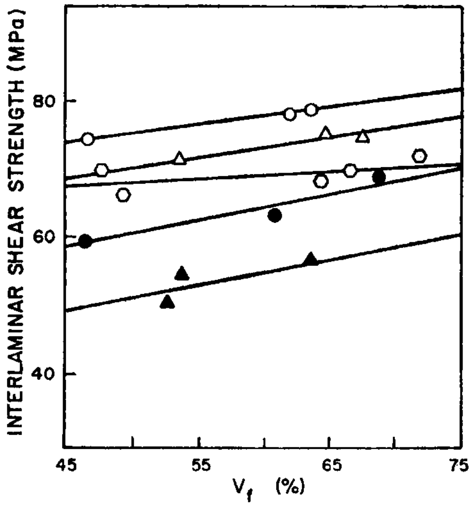

FIGURE 4 Variation of interlaminar shear strength of epoxy composites with volume fraction of graphite fibers coated by electropolymerization of different monomers: □, acrylic acid; △, diacetoneacrylamide; ●, methylmethacrylate; ▲, styrene-co-acrylonitrile; and ○, uncoated Hercules AU fiber.

It was expected that such surface modifications of carbon fibers can be accomplished by electrodeposition of preformed ionic polymers from solution or dispersion. For a number of copolymers containing carboxylic groups which could therefore be deposited on carbon fiber anodes,[13, 14] dramatic increases in the interlaminar shear strength of the composites were observed as a result of the electrodeposited polymer interphase. It is relevant to point out here that, in many systems studied, the increases in shear strength were also accompanied by simultaneous increases in impact strengths.[13, 14] This is in contrast to the usual observation that surface treatments, such as chemical oxidation, of carbon fibers which improve fiber-matrix adhesion and shear strength also bring about brittle fracture and lowered impact strengths in the composites.

Interphase modification by the electrodic processes described here therefore offers a method for optimization of composite shear and impact strengths. Additionally, it is also possible to investigate by these methods the molecular parameters of the interphase that are critical to optimum reinforcement. The molecular weight, chemical composition of polymers and copolymers, type and length of side chain groups, and crosslinking are among the molecular features that have been shown in our studies to control the extent of interphase modification.[5, 13, 14]

TABLE I

Dependence of interlaminar shear strengths of graphite fiber composites[a] on electroinitiated polymer coating

Electropolymerization system[b]	V_f %	Interlaminar shear strength MPa	Interlaminar shear strength σ^c
None (AU)[d]	47.5	69.5	0.86
	49.3	65.6	1.9
	64.5	68.1	2.2
	67.0	69.9	0.69
	72.0	71.6	1.2
Diacetoneacrylamide/H_2SO_4	54.9	71.7	0.59
	65.0	75.7	1.8
	68.0	75.2	1.7
Methyl methacrylate/$NaNO_3$–DMF	47.0	61.3	3.3
	61.8	63.8	1.3
	69.8	70.0	1.1
Styrene-acrylonitrile/$ZnCl_2$–CH_2Cl_2	40.5	42.3	1.0
	46.3	57.0	4.7
	53.0	51.0	1.2
	54.3	54.5	1.6
	64.0	57.5	1.7
Acrylic acid/H_2SO_4	46.8	73.6	2.1
	62.3	78.2	2.2
	64.0	79.0	5.0
	69.8	61.2	2.5

[a] Epoxy matrix resin.
[b] 2.5 sec polymerization.
[c] Standard deviation.
[d] Hercules AU untreated fiber.

4. SUMMARY

It is shown that polymer coatings can be formed on carbon fiber electrodes by electropolymerization of a variety of monomers. Single fiber pull-out tests seem to indicate three distinct modes of failure and degrees of adhesion of the coated fibers to an epoxy matrix: strong, intermediate and poor, which are independent of the types of polymer coating on the fiber. A significant feature of the results is the observation of the formation of a resin "cone" around the fiber, energy for which is needed to be expended before fiber pull-out can occur. In contrast to the fiber pull-out tests, interlaminar shear tests of composites prepared from the coated fibers reveal specific influences of the molecular features of the interphase polymer on composite properties.

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References

1. B. L. Funt and J. Tanner, *Tech. Chem.* (*N.Y.*) **5**, 559 (1975).
2. G. G. Shapoval and A. V. Gorodyskii, *Usp. Khim.* **42**, 854 (1973).
3. J. W. Breitenbach, O. F. Olaj and F. Sommer, *Fortschr. Hochpolym. Forsch.* **9**, 47 (1972).
4. James J. Jakubowski, "Interface Modification of Carbon Fiber Composites by Electropolymerization", Thesis, Washington State University (1976).
5. R. V. Subramanian and James J. Jakubowski, *Polym. Eng. Sci* (in press).
6. G. V. Shiriajeva and G. D. Andreevskaya, *Plastmassy* **4**, 43 (1962).
7. G. D. Andreevskaya, Yu. A. Gorbatkina, 25th Ann. Tech. Conf. SPI Reinf. Plastics/Composite Div., 16F (1970).
8. R. H. Norman, D. I. James and G. N. Cole, *Chem. Eng.* **182**, 243 (1964).
9. J. P. Favre and J. Perrin, *J. Mater. Sci.* **7**, 1113 (1972).
10. J. F. Bacon, "The Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems and Their Application to the Origination of High Modulus Glass Fibers", Final Report Contract NASW-1301 and NASW-2013 (1971).
11. R. D. Schile and G. A. Rasica, *Rev. Sci. Instruments* **38**, 1103 (1967).
12. R. V. Subramanian, H. F. Austin and T. J. Y. Wang, "Basalt Fibers", Final Report. Contract #NR-3017. Pacific Northwest Regional Commission (1976).
13. V. Sundaram, "Electrodeposition of Polymers on Carbon Fibers: Effects on Composite Properties", Thesis, Washington State University (1977).
14. R. V. Subramanian, A. K. Patel and V. Sundaram, Proc. SPI Reinforced Plast/Comp Inst. (1978), 20F.