Grafting of a Functionalized Side-Chain Liquid Crystal Polymer on Carbon Fiber Surfaces: Novel Coupling Agents for Fiber/Polymer Matrix Composites

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We studied covalent grafting to functionalized carbon fibers of a specially designed liquid crystalline monomer and its corresponding side-chain liquid crystalline polymer containing pendant chemical functions on their mesogenic groups. From a materials point of view these liquid crystalline compounds could act as coupling agents at fiber/polymer matrix interfaces, offering a mechanism to control composite properties not only through bonding but also through their "spontaneous" molecular orientation in interfacial regions. The grafting methodology for both monomer and polymer to fiber surfaces involved esterification through carbodiimide chemistry in solution. Carboxylic acid groups found on functionalized carbon fiber surfaces were esterified to phenolic functions in the side chains of the experimental polymer. Following grafting procedures the fibers were analyzed by scanning electron microscopy (SEM) and by contact angle measurements. SEM micrographs of fibers grafted with polymer revealed the presence of strongly attached polymeric material on the graphitic surface after rigorous extraction with polymer solvent. Contact angle measurements and polar/dispersive free energy analysis indicated also a smaller polar component of the surface free energy of fibers possibly due to the hydrophobic polymer backbone grafted on the carbon surfaces. On the basis of results, it is concluded that the esterification reaction grafted the polyphenolic liquid-crystal polymer on graphite fiber surfaces.

Introduction

Composite materials containing carbon fibers and polymeric matrices are used as structural components in many applications. The outstanding mechanical properties of these composites depend on the ability of the matrix to transfer stresses to the reinforcing material. It is recognized that this stress transfer from matrix to fiber requires ideally the formation of interfacial covalent bonds. Surface oxidation and fiber sizing were the only treatments of carbon fibers that resulted in the significant improvement of adhesion at the fiber–matrix interface.[1–5] There has been little work carried out on coupling agents for carbon fibers. Harris et al.[6] treated carbon fibers with boiling nitric acid and treated some of them with (β-(3,4-epoxycyclohexyl)ethyl)trialkoxysilane and some with (γ-glycidoxypropyl)trialkoxysilane. Mechanical testing of composites prepared with these treated fibers with a polyester resin showed a 23% improvement in shear strength with the oxidized fibers relative to unoxidized fibers and a further improvement of 10% with silane-treated fibers. The authors assumed the silanes acted as coupling agents through reaction with OH groups on the surface of the oxidized carbon fibers and groups in the matrix material. Other studies on improvement of interfacial adhesion in composites involved in situ polymerization of monomers which can react with fiber surface chemical functions. Koschinski and Reichert[7] used this approach in an attempt to modify poly(phenylene sulfide)/carbon fiber composite properties. They observed improved fiber/matrix adhesion and an increased resistance to corrosive media. Zeng and Bailing[8] investigated in situ polymerization of nylon 10,10 in the presence of carbon fibers but obtained poor properties in composite specimens. This was attributed by the authors to the low molecular weight of the matrix material. Bhama and Stupp investigated covalent grafting of main chain liquid crystal polymers on carbon fiber surfaces,[9] and this led to improved wetting and interfacial bonding of the liquid-crystalline matrix on carbon fibers. This finding motivated the present study involving a functionalized side-chain liquid-crystal polymer and its corresponding monomer acting as coupling agents for carbon fibers.

The synthesis and characterization of the thermotropic monomer and polymer studied here were reported previously by our laboratory.[10] The novel molecules have a phenolic functionality at the terminus of their mesogenic side groups which can react with carboxyl groups on carbon fibers and oxirane rings in epoxy resins. Therefore the reinforcing fiber can be, in principle, covalently bonded to the matrix. Moreover, studies in our laboratory revealed a strong tendency for these molecules to self-assemble into oriented arrays on both glass and carbon surfaces.[11] This property suggests that these compounds may form highly

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(1) Cooke, T. F. *J. Polym. Eng.* **1987**, *7* (3), 197.

(2) Drzal, L. T.; Rich, M. J.; Lloyd, P. M. *J. Adhesion* **1982**, *16*, 1.

(3) Fraser, W. A.; Ancker, F. H.; DiBenedetto, A. T. *Proc. of 1975 Conf. of RP/Composites Inst.*, Paper 22-A, **1975**.

(4) Goan, J. C.; Joo, L. A.; Sharpe, G. E. *Proc. of 1972 Conf. of RP/Composites Inst.*, Paper 21-E, **1972**.

(5) Drzal, L. T.; Rich, M. J.; Koenig, M. F.; Lloyd, P. M. *J. Adhesion* **1983**, *16*, 133.

(6) Harris, B.; Beaumont, P. W. R.; Rosen, A. *J. Mater. Sci.* **1969**, *4*, 432.

(7) Koschinski, I.; Reichert, K. H. *Makromol. Chem. Rapid. Commun.* **1988**, *9* (5), 291.

(8) Zeng, H.; Bailing, K. In *Composite Interphases*; Ishida, H., Koenig, J. L., Eds.; Elsevier: Amsterdam, 1986.

(9) Bhama, S.; Stupp, S. I. *Polym. Eng. Sci.* **1990**, *30* (10), 603.

(10) Bhama, S.; Stupp, S. I. *Macromolecules*, in press.

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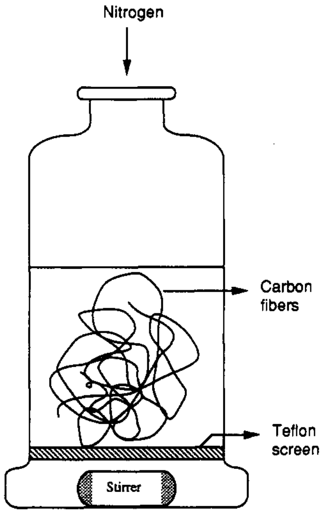


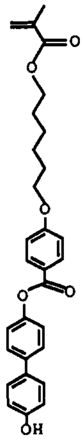
Figure 1. Schematic representation of the flask designed for the grafting reactions.

ordered boundary zones around fibers that would improve environmental stability and the physical properties of processed composites.

In this work we studied grafting of the liquid crystalline polyphenolic polymer and its monomer to functionalized carbon fibers by mild carbodiimide esterification reactions. The impact of the grafted molecules on surface properties of the fibers was investigated by scanning electron microscopy (SEM) and contact angle measurements.

Experimental Section

Grafting Reactions. A special flask was designed for our grafting reaction in order to avoid fracture of the fibers during magnetic stirring. A schematic drawing of this flask is shown in Figure 1. The round Teflon "screen" avoided any contacts between the stirrer and the fibers, and at the same time the holes in that screen were drilled large enough to allow effective stirring of the solution containing the fibers. All glassware was oven dried overnight; solvents were dried by refluxing over an appropriate drying agent, fractionally distilled, and stored over 4-Å molecular sieves. The catalyst 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) was synthesized according to the procedure described by Moore and Stupp.[12] The liquid crystal monomer and polymer were synthesized in our laboratory, and the preparation of both is described in detail in ref 10. The chemical structures of these molecules are as follows:



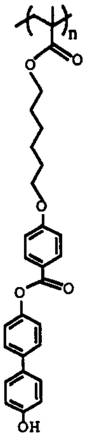
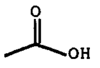


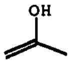
Table I. Solubility of Reactants in Grafting Reactions[a]

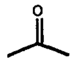
compound	solvent CH_2Cl_2	 THF	 DMF
monomer	s	s	s
polymer	i	s	s
DPTS	s	i	s
DCC	s	s	s

[a] s, soluble; i, insoluble.

The functionalized carbon fibers (AS4 12K from Hercules, Inc.) are expected to have a range of active functional groups on their surface such as







These functional groups have been introduced by oxidizing treatments such as heating in oxygen or treatment with nitric acid.[13,14] However, the carboxylic acid groups have been shown to be the most abundant.[15] To design the grafting reactions, the solubilities of various reagents were tested and reported in Table I. Dimethylformamide (DMF) was thus used for the grafting reaction of the monomer, and a mixture of 4 to 1 of dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) was used for the grafting of polymer.

The specially designed flask equipped with a Claisen adapter and a nitrogen inlet was charged with the phenolic monomer (0.038 g, 0.080 mmol), 0.015 g of carboxy-functionalized carbon fibers, DPTS (0.0048 g, 0.016 mmol), 1,3-dicyclohexylcarbodiimide (DCC, 0.0247 g, 0.120 mmol) and dry DMF. The volume of solvent used was large enough to ensure complete wetting of the fibers. The reaction flask was thoroughly purged with nitrogen and the contents were stirred under a nitrogen atmosphere overnight at room temperature. Fibers were then washed with THF, transferred to a Soxhlet extractor, and subjected to extraction with THF for 24 h. Following extraction, the fibers were dried overnight in vacuo at room temperature. A control experiment was carried out under similar conditions in the absence of the reagent DCC.

The procedure for grafting of polymer is identical to that of monomer except of course that phenolic polymer (0.038 g) was used. The polymer was first dissolved in a minimum amount of THF and transferred into the flask. A solvent mixture of about 40 mL of CH_2Cl_2 and 9 mL of THF was required in order to keep the polymer in solution. A control experiment was carried out under similar conditions in the absence of the polymer.

Analysis of Fibers. Treated fibers were analyzed by scanning electron microscopy (SEM) and contact angle measurements. SEM micrographs were obtained using a Hitachi S-800 scanning electron microscope. Fiber samples for SEM analysis were cut with a blade and their surfaces were sputtered with gold prior to microscopic analysis. Contact angles were measured using the gravimetric micro-Wilhelmy technique[16,17] shown schematically in Figure 2. A small length of the fiber studied was cut with tweezers and adhered to the end of a small hand-made copper wire hook with a fast curing epoxy adhesive. The fiber/hook was suspended on the arm of a Perkin-Elmer autobalance (Model AD-4) which had an accuracy of 1 μg. A very small beaker containing the liquid was slowly raised to the fiber tip using a custom-made jack. One turn of the knob of the jack corresponded to a rise of 0.254 mm. As soon as the fiber tip touched the liquid the microbalance would detect a change in force due to the wetting of the fiber by the liquid. The liquid was raised an additional 0.5 mm ($\sim$2 turns of the knob) in order to avoid fiber end effects on the measured data. This force was recorded, and six to ten measurements were made for each liquid. The reference liquids used in our study were water, glycerol, formamide, hexadecane,

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[11] Bhama, S.; Stupp, S. I. *Liquid Crystal Polymers with Functionalized Side Chains: Phase Transitions and Ordering on Fiber Surfaces*, submitted for publication.

[12] Moore, J. S.; Stupp, S. I. *Macromolecules* **1990**, *23*, 65.

[13] Mckee, D. W.; Memeault, V. J. *Chem. Phys. Carbon* **1973**, *9*, 151.

[14] Dauksys, R. J. *J. Adhesion* **1973**, *5*, 211.

[15] Drzal, L. T.; Rich, M. J.; Lloyd, P. F. *J. Adhesion* **1982**, *16*, 1.

[16] Hammer, G. E.; Drzal, L. T. *Appl. Surf. Sci.* **1980**, *4*, 340.

[17] Kaelble, D. H.; Dynes, P. J.; Cirlin, E. H. *J. Adhesion* **1974**, *6*, 23.

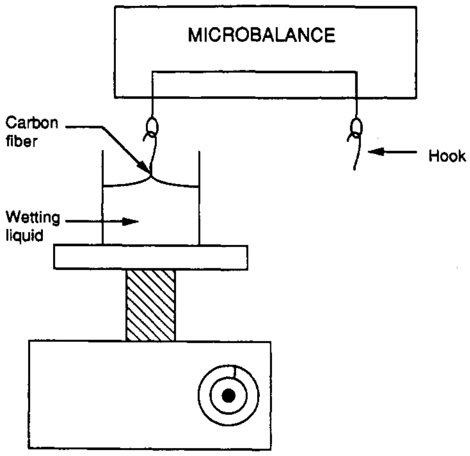


Figure 2. Schematic diagram of the device used in the micro-Wilhelmy technique for measurements of contact angle.

Table II. Surface Free Energy Components of Reference Liquids

liquid	γ_L^T (mJ/m^2)	γ_L^D (mJ/m^2)	γ_L^P (mJ/m^2)
water	72.8	21.8	51.0
glycerol	64.0	34.0	30.0
formamide[a]	58.3 (58)	32.3 (39)	26.0 (19)
polypropylene glycol[b]	31.3	24.5	6.8
n-hexadecane	27.6	27.6	0

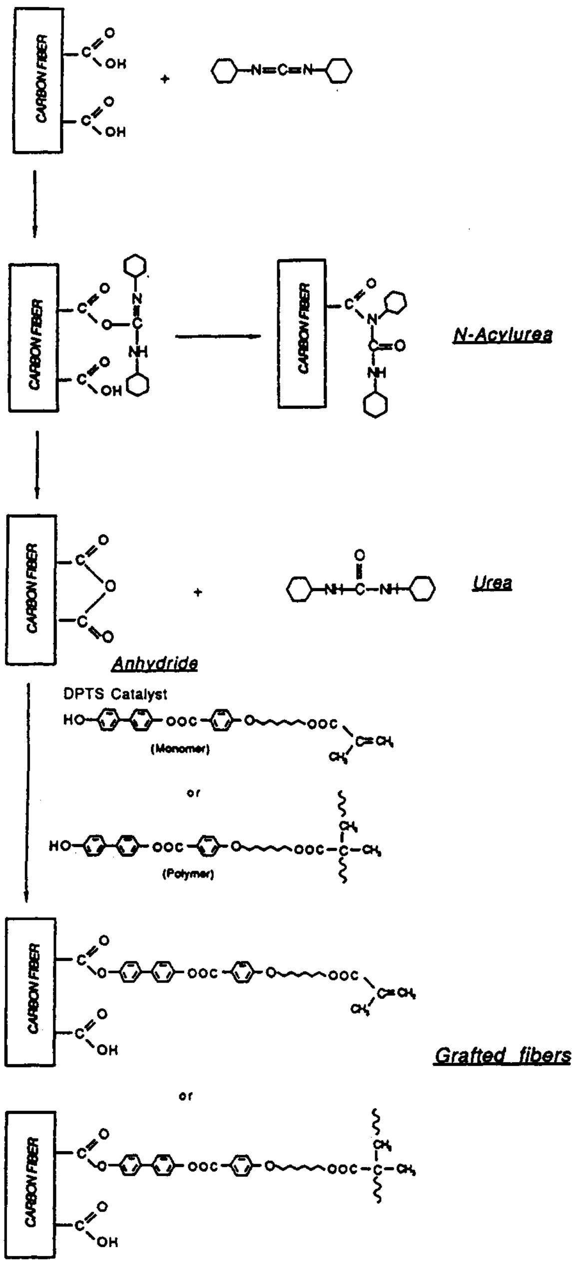
[a] The surface energy values in parentheses are also reported in the literature.[24] We used both values in our calculations of fiber surface energies and reached similar conclusions with regard to grafting on fibers (see text). [b] Molecular weight: 1200.

and polypropylene glycol. Their surface free energy components are listed in Table II.[16]

Results and Discussion

The reaction scheme of the grafting reaction is shown in Scheme I. Reaction of the carbodiimide with carboxylic acid groups results in the formation of an anhydride and urea. The acylation of the phenolic group by the acid anhydride is then catalyzed by DPTS which also suppresses the formation of *N*-acylurea. It has been reported by Moore and Stupp that the use of dichloromethane as a solvent gives better yields than DMF.[12] The important advantages of this esterification are that it is done under extremely mild conditions (room temperature, near-neutral pH, reaction in solution) and preactivation of the acid component is not necessary. The main drawbacks are that this reaction requires rigorous anhydrous conditions and proceeds only in selected solvents. The grafting of the liquid crystal monomer and polymer by this esterification reaction was designed for participation of the carboxyl groups present on carbon fiber surfaces. Therefore, to ensure good exposure of fiber surfaces to the experimental polyphenolic polymer the reaction was carried out in solution using only a small volume fraction of fibers. Moreover, according to Moore and Stupp[12] when DPTS is used as catalyst the esterification reaction gave yields approaching 90%. Therefore we expect that the grafting reactions attempted would result in monomer molecules and polymer chains covalently bonded to the carbon surface. However, since the distribution of carboxylic acid groups on functionalized carbon fiber surfaces is not a well-defined parameter, we cannot predict how evenly the surfaces would be covered by the coupling agents. Some investigators have conducted X-ray photoelectron spectroscopy (XPS) to provide atomic and molecular information about graphite fiber surfaces and infer that the surface oxygenated species are primarily carboxylic acid groups that exist preferentially at the edges and defect sites of the basal planes.[18,19]

Scheme I



Figures 3 and 4 show SEM micrographs of the untreated, as received functionalized carbon fibers, and of the functionalized carbon fiber exposed to the grafting reaction with monomer followed by soxhlet extraction with monomer solvent (THF). The micrographs in Figures 5 and 6 correspond to functionalized carbon fibers subjected to Soxhlet extraction after they had been grafted with polymer and to their corresponding control fibers, respectively. The control fibers have undergone exactly the same chemical treatment as the grafted ones except that polymer was not added to the reaction medium. The monomer-grafted fibers reveal a smooth surface and look similar to the surface of the as-received functionalized

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(18) Larsen, J. V.; Smith, T. G.; Erickson, P. W. *Carbon Fiber Surface Treatments*, NOLTR-71-165, 1971.

(19) Rand, B.; Robinson, R. *Carbon*, **1977**, *15*, 257.

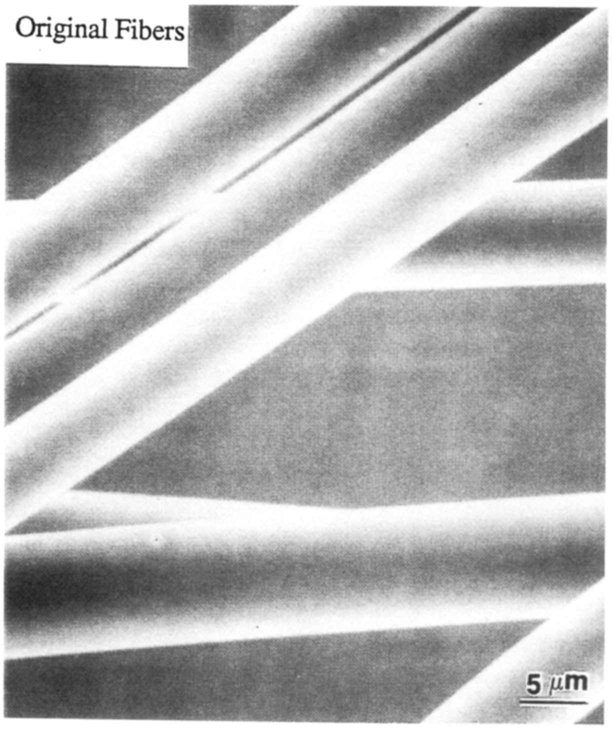

Figure 3. Scanning electron micrograph of carbon fibers prior to grafting.

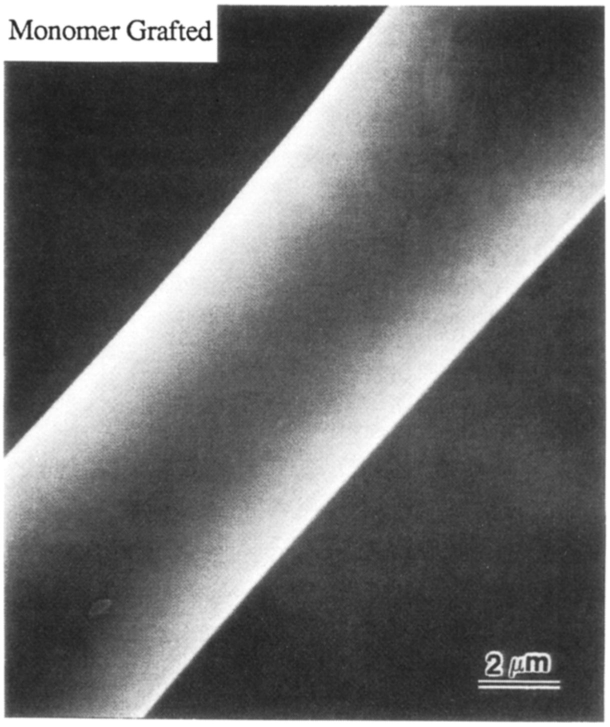

Figure 4. Scanning electron micrograph of a carbon fiber subjected to the grafting reaction with monomer and then exposed to Soxhlet extraction with THF, a solvent for the monomer.

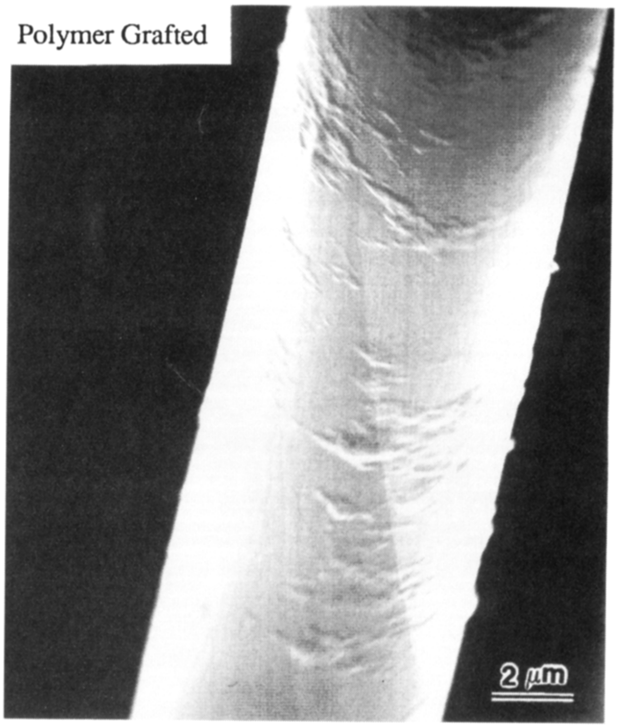

Figure 5. Scanning electron micrograph of a carbon fiber subjected to the grafting reaction with polymer and then exposed to Soxhlet extraction with THF, a solvent for the polymer.

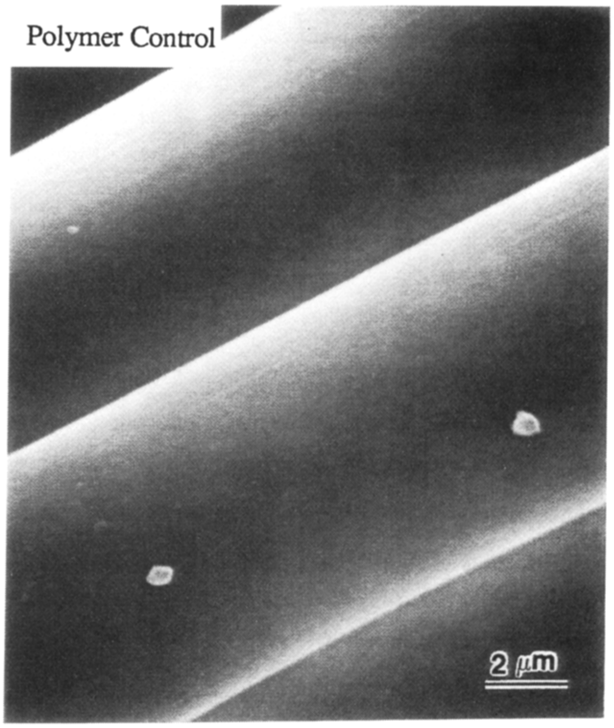

Figure 6. Scanning electron micrograph of carbon fibers serving as controls of fibers grafted with polymer. These fibers were subjected to the grafting reaction without using the polymer and then exposed to Soxhlet extraction with THF.

carbon fiber. However surfaces of fibers grafted with polymer revealed a rougher texture relative to all other fibers and seem to be covered with organic material. The process of Soxhlet extraction, to which fibers were exposed after the grafting reaction, would only remove physisorbed molecules. This strongly suggests that the material left on fiber surfaces after rigorous Soxhlet extraction indeed contains covalently grafted comb macromolecules as well as entangled ones with those grafted. Fiber weight gain measurements could have offered additional evidence for grafting of monomer or polymer or carbon fibers. However this was not feasible in our study given the loss of fiber weight on filters during the Soxhlet extraction.

A modification of the surface chemical composition of the functionalized carbon fibers could change their polarity. To establish if such changes occurred we measured polar/dispersive surface free energies through contact angles. According to the method proposed by Hammer

Table III. Contact Angles (deg) of Various Liquids on Carbon Fibers

liquid	original fiber	control for monomer[a]	monomer grafted	control for polymer[b]	polymer grafted
water	74 ± 2	49 ± 4	47 ± 4	53 ± 5	70 ± 4
glycerol	59 ± 3	63 ± 2	61 ± 2	47 ± 1	56 ± 6
formamide	38 ± 4	49 ± 5	47 ± 5	37 ± 4	47 ± 7
PPG	25 ± 8	48 ± 6	35 ± 9	26 ± 5	24 ± 5
hexadecane	29 ± 7	32 ± 4	30 ± 5	27 ± 5	29 ± 5

[a] These fibers were subjected to the grafting reaction without using the critical carbodiimide reagent and then exposed to Soxhlet extraction with THF. [b] These fibers were subjected to the grafting reaction without using the polymer and then exposed to Soxhlet extraction within THF.

and Drzal[16] and Kaelble et al.[17] the total surface free energy γ^T for a liquid (γ_L^T) or a solid (γ_S^T) is composed of Keesom polar (γ^P) and London dispersion (γ^D) components:

$$\gamma_L^T = \gamma_L^P + \gamma_L^D \qquad (1)$$

$$\gamma_S^T = \gamma_S^P + \gamma_S^D \qquad (2)$$

The work of adhesion[20,21] is given by

$$W_A = \gamma_L^T(1 + \cos\theta) \qquad (3)$$

Using eqs 1–3 and rearranging, we get

$$\gamma_L(1 + \cos\theta)/2(\gamma_L^D)^{0.5} = (\gamma_S^D)^{0.5} + (\gamma_S^P)^{0.5}(\gamma_L^P/\gamma_L^D)^{0.5} \qquad (4)$$

where γ_L^P and γ_L^D are known for the liquids used to wet the fibers and θ is measured. A plot of $\gamma_L(1 + \cos\theta)/2(\gamma_L^D)^{0.5}$ versus $(\gamma_L^P/\gamma_L^D)^{0.5}$ yields a straight line, and the slope and intercept provide the values of γ_S^P and γ_S^D for the carbon fibers studied. The force measured by the micro-Wilhelmy technique could be related to contact angle through the following expression:[22,23]

$$F = \gamma_L \pi d \cos\theta \qquad (5)$$

where γ_L is the surface free energy of the liquid, d the diameter of the fiber, and θ the advancing liquid/solid contact angle. A diameter of 8 μm was assumed for all the fibers investigated. Knowing F, γ_L, and d, cos θ can be calculated and substitution in eq 4 gives the polar and dispersive components of the fiber's surface free energy.

Contact angle data are shown in Table III. The values of θ listed were calculated from eq 5 and represent the average of measurements made on each type of fiber with the indicated liquid. It was anticipated that the contact angle measured with a polar liquid would be small for a relatively hydrophilic surface due to good wetting and vice versa. In general, contact angles decrease with decreasing surface tension of the liquids. The values determined for the monomer-grafted fibers and their corresponding control fibers are approximately similar. However, the contact angles measured on polymer grafted fibers are greater compared to those of control fibers. Plots based on eq 4 are shown in Figures 7 and 8 including linear regression analysis to determine the best straight-line fit for each data set. The slope and intercept of these lines provide the polar (γ_S^P), dispersive (γ_S^D) and total (γ_S^T) surface free energies for each type of fiber. These results are given in Table IV. Comparing values of the total surface free energy γ_S^T shows that generally surface treatments increase γ_S^T except in the case of polymer-grafted fibers. Fibers grafted with monomer and their controls exhibit similar γ_S^T, whereas fibers grafted with polymer have a significantly lower γ_S^T compared to control fibers. A comparison of the polar (γ_S^P) and dispersive (γ_S^D) components of the surface free energy indicates that the original fibers have the most hydrophobic surface. At the same time γ_S^P and γ_S^D are approximately the same for the fiber grafted with monomer and its control. A striking

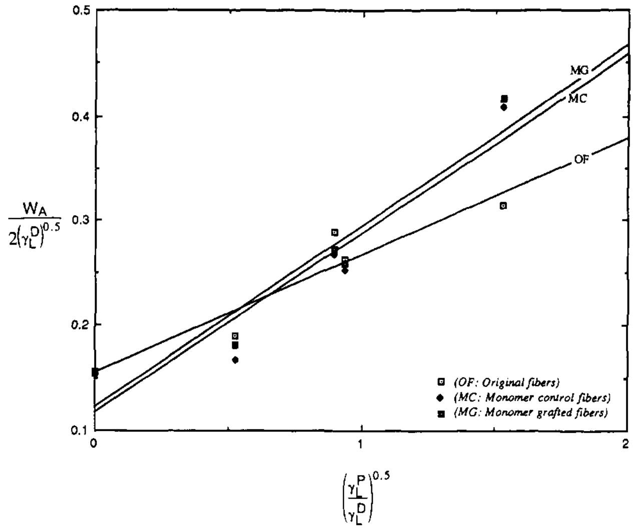

Figure 7. Plots of $W_A/2(\gamma_L^D)^{1/2}$ versus $(\gamma_L^P/\gamma_L^D)^{1/2}$ for fibers grafted with monomer (MG), the corresponding control fibers (MC), and original fibers (OF). Linear regression analysis lead to the following equations: $y = 0.155 + 0.112x$ ($R^2 = 0.896$) for OF, $y = 0.117 + 0.170x$ ($R^2 = 0.893$) for MC, and $y = 0.122 + 0.173x$ ($R^2 = 0.913$) for MG.

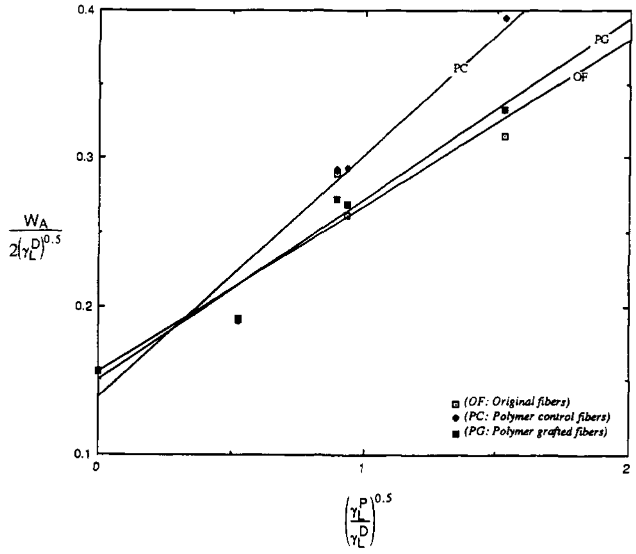

Figure 8. Plots of $W_A/2(\gamma_L^D)^{1/2}$ versus $(\gamma_L^P/\gamma_L^D)^{1/2}$ for fibers grafted with polymer (PG), the corresponding control fibers (PC), and original fibers (OF). Linear regression analysis lead to the following equations: $y = 0.155 + 0.112x$ ($R^2 = 0.896$) for OF, $y = 0.138 + 0.164x$ ($R^2 = 0.955$) for PC and $y = 0.149 + 0.122x$ ($R^2 = 0.961$) for PG.

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(20) Kaelble, D. H. *Physical Chemistry of Adhesion*; Wiley-Interscience: New York, 1971.

(21) Kaelble, D. H. *Proc. 23rd Int. Cong. of Pure Applied Che.*, **1971**, *8*, 265.

(22) Neumann, A. W.; Tanner, W. *Proc. 5th Int. Cong. on Surface Activity*, **1968**, *2*, 727.

(23) Mozzo, G.; Chabord, R. *Proc. 23rd Annual Conf., Reinforced Plastics/Composites Division*, Soc. Plastics Industry, 1968, Section 9-C, 1.

(24) Dann, J. R. *J. Colloid Interface Sci.* **1970**, *32* (2), 302.

Table IV. Polar, Dispersive, and Total Surface Free Energies[a] of Carbon Fiber Surfaces

fiber	γ_S^P (mJ/m^2)	γ_S^D (mJ/m^2)	γ_S^T (mJ/m^2)
original fiber	12.6 (10.4)	23.9 (28.3)	36.5 (38.7)
control for monomer[b]	29.0 (26.0)	13.6 (18.7)	42.6 (44.7)
monomer grafted	29.9 (27.1)	14.9 (19.1)	44.8 (46.2)
control for polymer[c]	26.7 (23.7)	19.0 (24.1)	45.7 (47.8)
polymer grafted	14.9 (13.1)	22.2 (25.8)	37.1 (38.9)

[a] The surface energy values in parentheses were obtained when data for polypropylene glycol (PPG) are excluded from curve fitting procedures (see text). [b] These fibers were subjected to the grafting reaction without using the critical carbodiimide reagent and then exposed to Soxhlet extraction with THF. [c] These fibers were subjected to the grafting reaction without using the polymer and then exposed to Soxhlet extraction with THF.

difference is seen however in the polar components of fibers exposed to the polymer grafting reaction. The grafted fibers show roughly a 50% decrease in polarity, in other words the grafted fibers reveal a surface which is twice as hydrophobic as the control fibers. The surface energy values in parentheses were obtained when data for polypropylene glycol (PPG) are excluded from curve-fitting procedures. In Figures 7 and 8 note that the data points corresponding to PPG fall off the fitted curve and therefore lead to low intercept values (low γ_S^D's). The values in parentheses are higher and also the correlation factors in curve-fitting procedures are much closer to 1. However, both sets of values lead to the same conclusion regarding evidence for grafting.

Our results on surface free energy analysis indicate that the monomer-grafting reaction does not change the polarity of fiber surfaces. This observation suggests too little monomer is grafted on the carbon fiber to affect significantly the surface properties. Surface free energy analysis of polymer-grafted fibers reveals a very hydrophobic surface which one may attribute to the presence on the surface of the hydrophobic sectors of bound polymer. This is certainly consistent with the observation by SEM of extraction-proof adhered material on these fibers. Compared to the original carbon fibers the polymer grafted fibers exhibit a slightly higher γ_S^P which can be explained by the presence of phenolic groups in the polymer's side chains. However the overall effect of the strongly attached polymer is to create a more hydrophobic surface relative to the surface of control fibers.

Conclusions

A side-chain liquid crystal polymer functionalized with phenolic groups was grafted by esterification to carbon fiber surfaces. Examination of the fibers by SEM after the reaction revealed tenaciously attached material some of which is thought to be covalently bonded to the surface. Contact angle measurements on the fibers after grafting revealed a hydrophobic surface which is attributed to the polymer's backbone and its alkyl spacers. The bonded polyphenolic side chain liquid crystal polymer could serve as an effective coupling agent at carbon fiber–polymer interfaces given its potential to react with matrix materials and form thermally stable ordered regions.

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