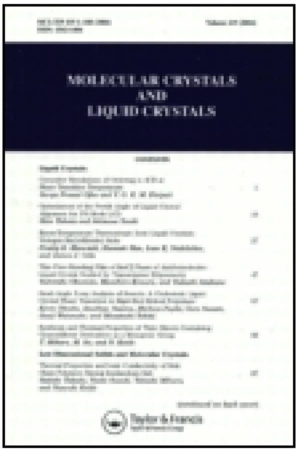

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Liquid Crystal Orientation on Carbon Fibers

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Liquid Crystal Orientation on Carbon Fibers

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The orientation of 4-methoxybenzylidene-4′-n-butylaniline (MBBA) on four different carbon fibers has been investigated by X-ray diffraction. The diffraction patterns show that the MBBA liquid crystal is oriented in the direction of the fiber for all of the fibers studied. Scanning electron microscopy (SEM) of the fiber surfaces reveals grooves along the fiber axis which may cause orientation of the MBBA. The degree of MBBA orientation seems independent of the size and parallelism of the grooves. These results suggest that the preparation of composites with oriented polymer matrices is possible by using liquid crystalline monomers.

Keywords: MBBA (4-methoxybenzylidene-4′-n-butylaniline), carbon fibers, liquid crystals, X-ray diffraction

INTRODUCTION

The orientation of liquid crystals by surface effects, magnetic fields and flow is well known and forms the basis for many of the most useful technological applications of liquid crystals. The mechanism of surface alignment has been the subject of numerous reports[1–4] and Cognard has provided a review[5] of liquid crystal alignment on a variety of surfaces including glasses, metals, oxides and polymers. The influence of surface grooving, surface active agents, and physiochemical interactions was discussed. Relatively few reports have discussed carbon surfaces, however. Zimmer and Weitz[6] examined the orientation of carbonaceous mesophase on carbon fibers in the presence of a magnetic field. Creagh and Kmetz studied[7] the alignment of MBBA on various surfaces, including carbon. Perpendicular, homogeneous parallel and random parallel alignment of MBBA on carbon was observed, depending on the surface treatment and surfactant present.

More recently, Bhama and Stupp[8,9] and Chung, Gurion and Stamatoff[10] have investigated the behavior of polymer liquid crystals in the presence of carbon fibers. These reports were concerned with the use of polymer liquid crystals as composite matrices. Chung, Gurion and Stamatoff prepared polymer liquid crystal/carbon fiber composites and demonstrated that the polymer liquid crystal became oriented parallel to the carbon fibers, regardless of initial orientation. Bhama and Stupp

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used nuclear magnetic resonance (NMR) spectroscopy to show that carbon fiber surfaces influenced the orientation and orientational dynamics of a liquid crystalline polymer matrix. They also grafted liquid crystal polymers onto carbon fiber surfaces by carrying out the polymerization reaction in the presence of functionalized fibers. Traditionally, unoriented polymers such as epoxy and polyester have been used as composite matrices. The use of an oriented polymer as a composite matrix could dramatically improve composite properties, particularly if the polymer was oriented transverse to the carbon fibers. Transverse alignment would allow the carbon fibers to support loads in one direction, and the oriented polymer to support loads in the transverse direction. Bhama and Stupp[11] have briefly discussed the advantages of transverse alignment.

We became intrigued with the potential of liquid crystal orientation by fiber surfaces, particularly after the recent work of Hoyt, Benicewicz and Huang[12–15] involving the synthesis of liquid crystal thermosets (LCT). They reported that low molecular weight liquid crystals with reactive endgroups could be polymerized to form a polymer in which the liquid crystalline order had been preserved by cross-linking. Other workers[16–19] have achieved similar results with mesogenic diacrylates. Since liquid crystalline polymers are oriented by carbon fibers, it is reasonable to expect carbon fibers to orient liquid crystalline monomers in a similar fashion. Subsequent polymerization of the oriented monomers in the presence of the carbon fibers would result in an oriented polymer matrix. If the monomers were aligned parallel to the fibers, transverse alignment of the polymer backbone could be accomplished by employing a polymerization mechanism that propagates transverse to the direction of monomer alignment. Alternatively, transverse alignment of the polymer could be attained by homeotropic (perpendicular) alignment of the monomers on the carbon fibers, followed by polymerization of the monomers in an end-to-end fashion.

The ultimate goal of our work is to demonstrate the ability to tailor the orientation of polymer matrices in composite materials. The pursuit of this goal involves two objectives: (1) the study of liquid crystal orientation on fiber surfaces and (2) the synthesis of appropriate liquid crystalline monomers. The present communication deals with the progress achieved thus far in pursuit of objective (1). No published reports concerning liquid crystal orientation on carbon fibers were found in a computerized search[20] of the literature. Therefore, the current work has focused on the orientation of a common liquid crystal, MBBA, in the presence of four commercially available carbon fibers with varying moduli and surface structure. X-ray diffraction has been used to characterize the fiber and MBBA orientation and scanning electron microscopy (SEM) was used to characterize the fiber surfaces.

EXPERIMENTAL

Unsized T-300, T-50, and P-55 carbon fibers were obtained from Amoco Performance Products. Unsized E-130 carbon fibers were obtained from DuPont. X-ray diffraction experiments were performed on single tows of fiber (approximately 3000 strands), approximately 4 cm in length and weighing 15–20 mg. An eyedropper was used to apply 15–20 mg of MBBA (Aldrich Chemical Co.) to each fiber tow. In a typical experiment, the MBBA was applied in a thin stream along the length of the fiber to minimize "wicking" or capillary action along the fiber. An X-ray diffraction photograph was then taken, and the fiber/MBBA prepreg was heated above the clearing temperature of MBBA (41°C) on a microscope slide. After cooling, another X-ray diffraction pattern was obtained to see if isotropization of the MBBA had changed the orientation.

Wide angle X-ray diffraction (WAXD) patterns were obtained with nickel filtered copper K_α radiation using a commercially available (Blake Industries) evacuatable flat plate camera with pin-hole collimation. X-rays were produced by a Philips Electronics XRG3100 generator operated at 45kV and 30mA. With a nominal sample to film distance in the camera of 5 cm, exposure times of 1.5 hours were typical.

RESULTS AND DISCUSSION

The identities of the four carbon fibers selected for these experiments are shown in Table I. The objective of these experiments is to study the effect of carbon fiber surface structure and orientation on MBBA orientation. Accordingly, fibers were selected with a broad range of modulus values and represent two different manufacturing processes, pitch-based and polyacrylonitrile-based (PAN-based). Both types of carbon fibers are composed of oriented graphitic layers and an increase in the orientation of the layers generally leads to increased fiber modulus. For a discussion of the manufacturing process of both types of fiber and of the effect of layer orientation on modulus, see Riggs, Shuford and Lewis.[21] The modulus values in Table I are thus indicative of the overall orientation of the carbon fibers. Figures 1–4 show 5000X SEM photos of the four fibers. All of the fibers show axial grooving of the fiber surface as a result of the manufacturing process. Pitch-based fibers such as E-130 and P-55 have shallow, narrow, highly parallel grooves whereas the grooves of the PAN-based T-50 and T-300 fibers are much deeper, wider and less oriented.

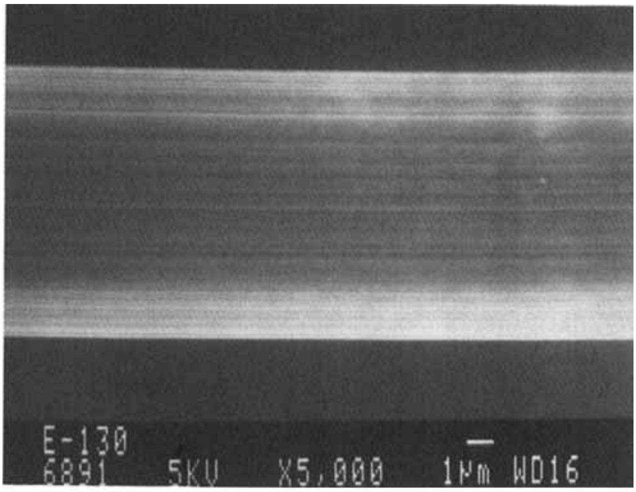
To investigate the possible link between surface grooving and liquid crystal orientation, the four fibers were impregnated with an approximately equal weight of MBBA to form "prepreg" tows. An effort was made to apply the MBBA with an eyedropper in a line along the surface of the fiber tows in order to reduce

TABLE I

Fiber identification

Fiber	Nominal modulus[a]	Manufacturing method
E-130	130	Pitch-based
T-50	57	PAN-based
P-55	55	Pitch-based
T-300	33.5	PAN-based

[a] Units are 10^6 lbf/in^2. The modulus values shown were provided by the manufacturer and no attempt at verification was made.



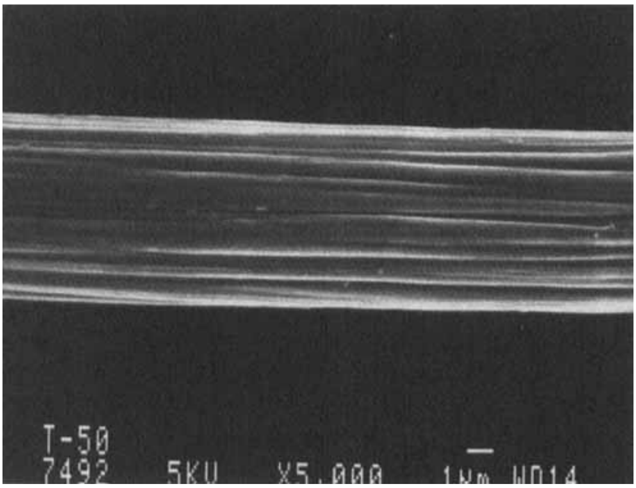


FIGURE 2 5000× SEM photo of a single T-50 fiber.

capillary effects, but some wicking still occurred. Figure 5 is a X-ray diffraction pattern of MBBA in a glass capillary showing that it is unoriented with a d-spacing of 4.6Å. Figure 6 shows the X-ray diffraction pattern of a bare E-130 fiber tow. The sharp equatorial (002) reflections indicate that the fibers are highly oriented. Figure 7 shows the X-ray diffraction pattern of an E-130/MBBA prepreg tow. The inner pair of arcs corresponds to the 4.6Å d-spacing of MBBA and indicates that the MBBA is oriented with the long axes of the molecules parallel to the fiber. The orientation is preserved even when the prepreg tow is heated above the isotropization temperature of the MBBA and cooled back to room temperature (heat/cool cycle), as shown in Figure 8.

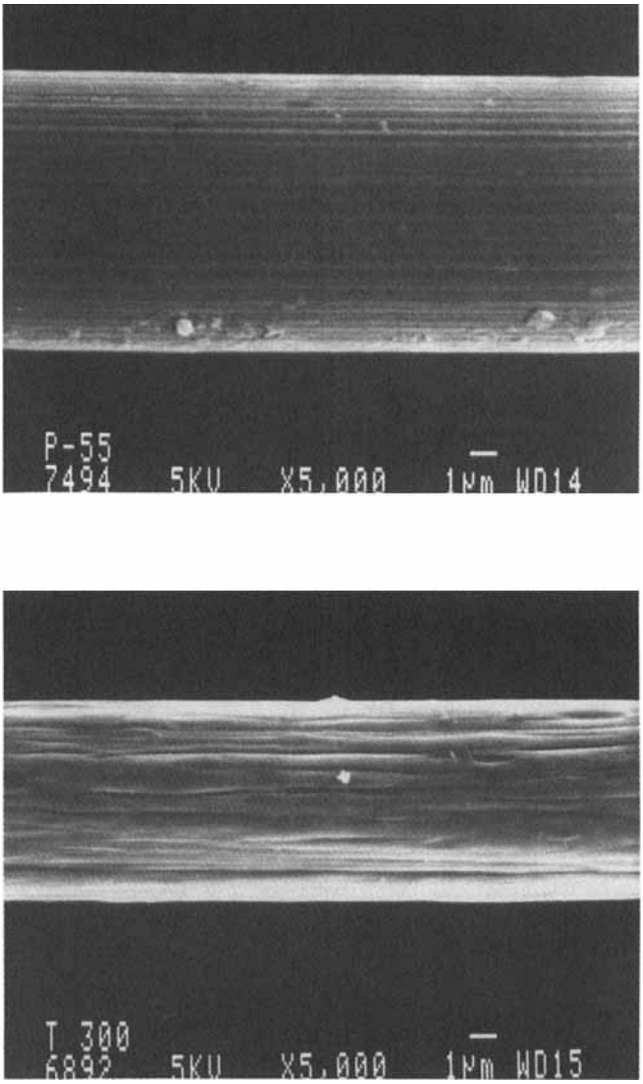


FIGURE 4 5000× SEM photo of a single T-300 fiber.

The X-ray diffraction patterns of the T-50/MBBA, P-55/MBBA and T-300/MBBA prepregs are shown in Figures 9, 10 and 11, respectively. In each case, the outer pair of equatorial arcs corresponds to the ~3.4Å d-spacing of the carbon fiber graphitic (002) planes. The X-ray diffraction patterns clearly show that the orientation of the fibers decreases in the order E-130 > T-50 ~ P-55 > T-300. The inner pair of arcs in each pattern corresponds to the 4.6Å d-spacing of MBBA. Surprisingly, the orientation of the MBBA is approximately the same in each pattern. The degree of orientation of the MBBA is preserved even after a heat/cool cycle. This is an unforeseen result, as we expected that either the fiber orientation or the surface groove orientation (or both) would affect the alignment of

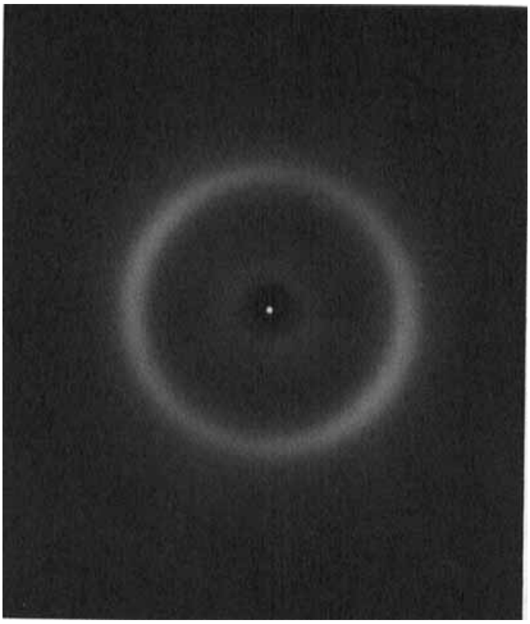


FIGURE 5 X-ray diffraction pattern of unoriented MBBA.

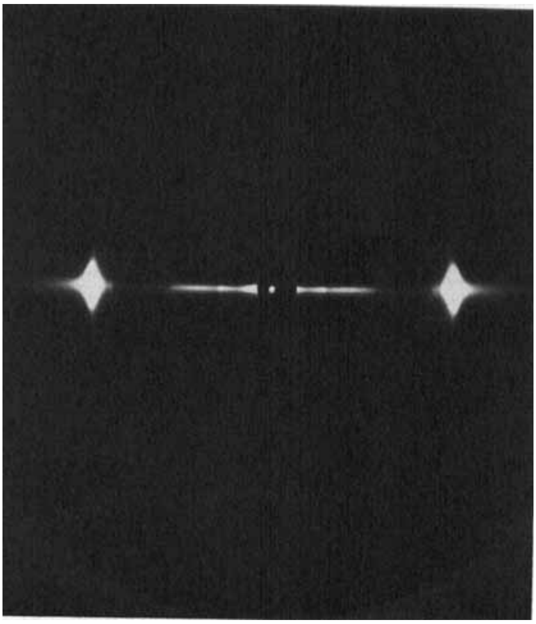


FIGURE 6 X-ray diffraction pattern of an E-130 fiber tow (fiber axis vertical).

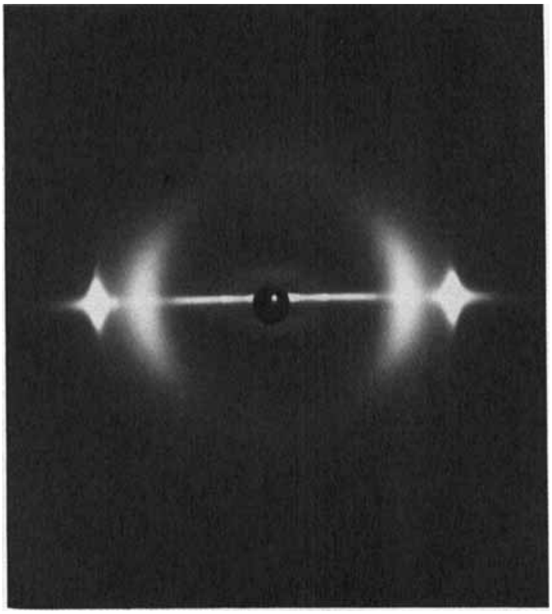


FIGURE 7 X-ray diffraction pattern of an E-130/MBBA prepreg (fiber axis vertical) at room temperature.

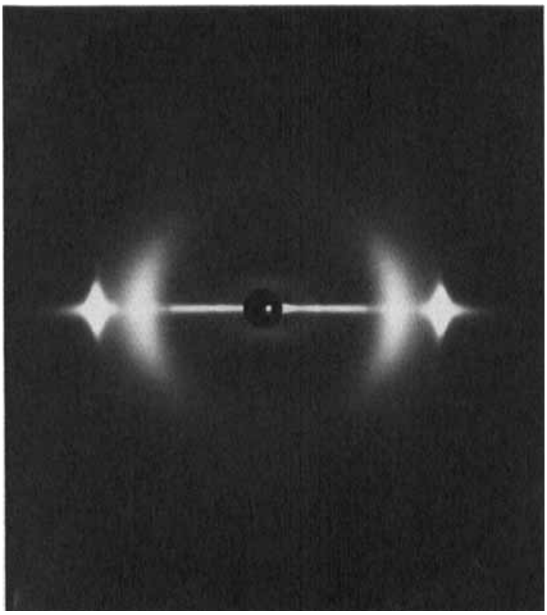


FIGURE 8 X-ray diffraction pattern of an E-130/MBBA prepreg (fiber axis vertical) at room temperature after MBBA isotropization.

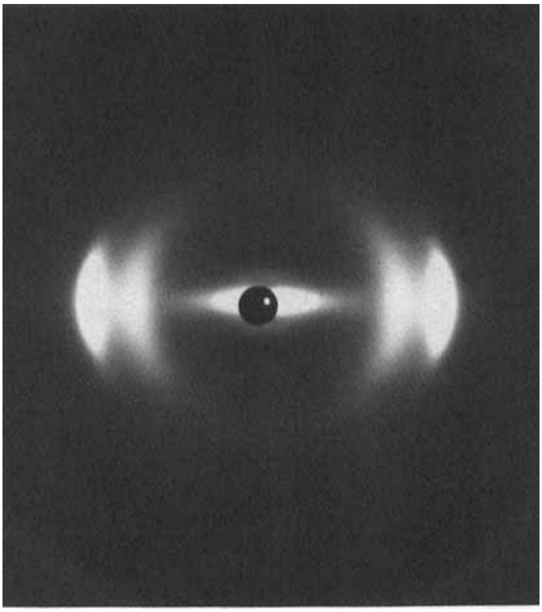


FIGURE 9 X-ray diffraction pattern of a T-50/MBBA prepreg (fiber axis vertical) at room temperature.

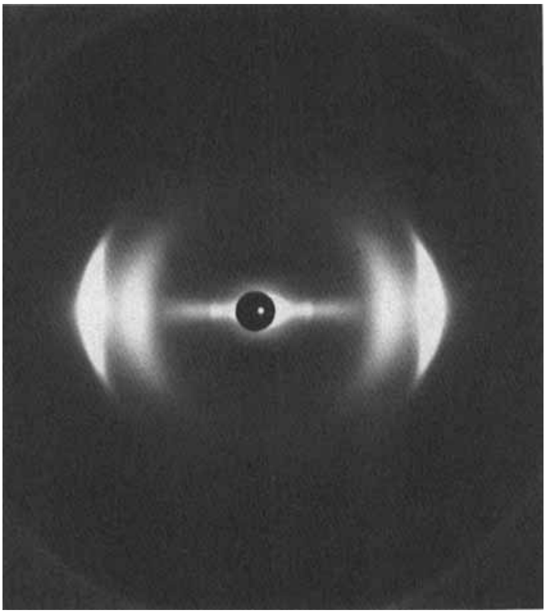


FIGURE 10 X-ray diffraction pattern of a P-55/MBBA prepreg (fiber axis vertical) at room temperature.

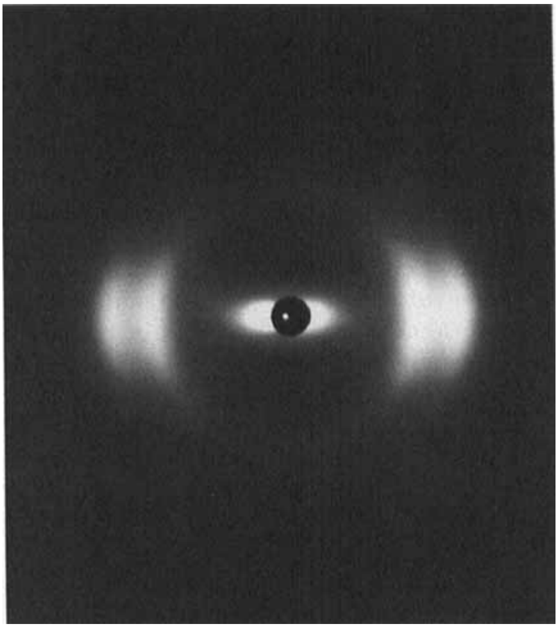


FIGURE 11 X-ray diffraction pattern of a T-300/MBBA prepreg (fiber axis vertical) at room temperature.

MBBA. Instead, the degree of orientation of MBBA in the presence of carbon fibers appears to be independent of the orientation of the graphitic layers within the fibers or of the linearity of surface grooving. Although more quantitative measures of the MBBA orientation may reveal a trend, there is no apparent correlation between fiber orientation and MBBA orientation. One reason may be that the liquid crystal is oriented by surface features too small to be imaged by SEM and that these features are the same for each fiber. Another possibility is that the liquid crystal is highly oriented at the surface, but that the tendency to remain oriented decreases as the distance from the surface increases. Thus, the overall orientation of the MBBA, as measured by X-ray diffraction, is the superposition of the oriented surface layers and the less oriented material occupying the space between the fibers. According to this mechanism, increasing the fiber surface orientation increases the orientation of MBBA near the surface, but has little effect on the bulk of the liquid crystal. The fact that the orientation is preserved after a heat/cool cycle lends support to the hypothesis that there is some surface anchoring of the liquid crystal on the carbon fiber.

Preliminary X-ray diffraction experiments have been conducted with MBBA and unoriented alumina fibers, which do not show surface grooving by SEM. Ambiguous results have been obtained in these early experiments as the MBBA is sometimes oriented and sometimes unoriented. These results indicate that some factor other than surface grooving is contributing to liquid crystal orientation. The observed alignment may be due in part to the capillary flow of the liquid crystal that takes place as the MBBA is applied to the fiber, as the orientation of liquid crystals by flow is well known.[22]

Regardless of the orientation mechanism, we believe that we have demonstrated for the first time that low molecular weight liquid crystals become oriented in the presence of carbon fibers. As noted previously, several workers have already prepared liquid crystal thermoset (LCT) materials. If carbon fibers are prepregged with these or similar liquid crystalline monomers, it is likely that the monomers will become oriented by the carbon fibers. Curing the monomers to produce an oriented polymer matrix could dramatically enhance the mechanical properties of the composite. The alignment of liquid crystals on surfaces has been studied in considerable detail and this knowledge base should be applicable to carbon fiber surfaces. By learning to manipulate the orientation of the monomers, we should be able to tailor the orientation of the resulting polymer matrix for specific applications. In general, the orientation of the resulting polymer will be different than the monomer because the polymerization vector is at some angle to the monomer axis. The type of phase exhibited by the monomer, the polymerization mechanism, fiber surface treatment, external fields and processing conditions are also expected to influence the orientation of the resulting polymer.

Future work in our laboratories will focus on extending these experiments to other liquid crystals and other fibers. It is hoped that experiments on unoriented fibers without surface grooving (such as the alumina fibers mentioned earlier) will distinguish between the influence of surface grooving and wicking on orientation. An ongoing synthetic effort will be continued to provide a source of liquid crystalline monomers.

CONCLUSION

The orientation of a low molecular weight liquid crystal, MBBA, has been characterized by X-ray diffraction in the presence of four different carbon fibers of varying moduli. The diffraction patterns clearly show that the long axis of MBBA molecules in MBBA/carbon fiber prepregs is oriented parallel to the fibers and that the degree of orientation is relatively insensitive to carbon fiber surface features or carbon fiber orientation. We hypothesize that the orientation is caused by a combination of capillary flow (wicking) and carbon fiber surface anchoring.

The orientation of MBBA on carbon fibers is a simple and inexpensive process. Liquid crystal monomers should orient on carbon fibers in a similar fashion, and subsequent polymerization is expected to lead to composites with oriented matrices. The ability to tailor the orientation of composite polymer matrices will represent a significant advance in the design of composite materials.

Acknowledgments

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