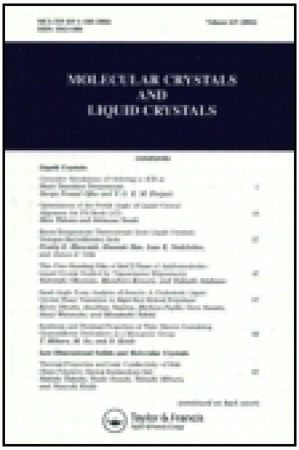

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Alignment of Nematic and Smectic A Liquid Crystals on Carbon, Organic and Inorganic Fibers

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Alignment of Nematic and Smectic A Liquid Crystals on Carbon, Organic and Inorganic Fibers

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The spontaneous alignment of nematic and smectic A liquid crystals on oriented and unoriented fibers has been investigated. The alignment of two nematic liquid crystals, 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA) and 4′-pentyl-4-biphenylcarbonitrile (5CB), and a commercial smectic A liquid crystal mixture, BN/75A, on a series of carbon, organic and inorganic fibers has been characterized by X-ray diffraction. We have discovered that all of the liquid crystals aligned uniformly parallel to the axes of oriented carbon and organic fibers (coaxial alignment), but were unaligned on the unoriented inorganic fibers. We hypothesize that the uniform alignment of the liquid crystals resulted from the influence of oriented microscopic grooves and/or oriented nanoscale features such as polymer crystallites or carbon fiber basal plane edges. All of the oriented fibers except Kevlar 49 have both surface grooves visible at 5000X and a high degree of molecular orientation. The alignment of the liquid crystals on Kevlar 49 may be caused by very small oriented fissures or voids in the skin of the fiber that are not visible at 5000X.

We suggest a route to composites with oriented polymer matrices by the in situ (in the presence of fibers) polymerization of uniformly aligned liquid crystalline monomers. The resulting composites should have superior mechanical properties relative to composites with unoriented matrices, particularly if transverse (perpendicular or tangential) alignment of the polymer backbones relative to the fiber axes can be achieved.

INTRODUCTION

The long axes of many rod-shaped liquid crystalline molecules can become uniformly aligned by contact with a properly treated substrate. Microscopic grooves and/or surfactants on the substrate surface strongly influence the degree and direction of alignment. For instance, rubbing a glass surface with diamond paste produces parallel grooves that induce uniform alignment of liquid crystals parallel to the surface, whereas prior treatment of the glass with a surfactant generally leads to perpendicular (homeotropic) alignment.[1–5] The uniform alignment of liquid crystals on various organic and inorganic substrates has been well studied, particularly with regard to applications involving liquid crystal display devices. In contrast, few reports have appeared concerning liquid crystal alignment on fiber surfaces. The alignment of rod-shaped liquid crystals on fiber surfaces can be defined

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in terms of the principle axes illustrated in Figure 1. Parallel[6] alignment of carbonaceous mesophase and coaxial alignment of *polymer* liquid crystals[7,8] on carbon fibers has been observed. We have previously[9] employed X-ray diffraction to investigate the alignment of 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA) on a series of four carbon fibers with different surface morphologies. Our results indicated that MBBA was coaxially aligned on all four fibers, but that the degree of alignment did not correlate with the degree of carbon basal plane orientation.

Our interest in this topic stems from a desire to prepare composite materials with oriented polymer matrices by the in situ (in the presence of fibers) polymerization of uniformly aligned liquid crystalline monomers. This concept for preparing oriented composite matrices emphasizes the use of *monomer* liquid crystals as opposed to previous approaches[7,8] utilizing *polymer* liquid crystals. Typical composite materials such as graphite/epoxy utilize carbon fibers in an unoriented epoxy matrix. The carbon fibers bear nearly all of the structural loads, whereas the epoxy transfers loads between fibers, protects the fibers and holds the fibers together. The epoxy does not carry structural loads because the modulus and strength of epoxy are lower by orders of magnitude than the strength and modulus of typical carbon fibers. However, the strength and modulus of highly *oriented* polymers are comparable to carbon fibers.[10] Previous attempts to utilize oriented polymers as composite matrices have encountered obstacles. Mechanical drawing of a viscous polymer melt, solution or gel to achieve orientation is very difficult in the presence of carbon fibers. This difficulty was partially circumvented by utilizing polymer liquid crystals which oriented easily and had relatively low viscosities, but coaxial alignment of the polymer liquid crystals was observed.[7,8] Ideally, the alignment of the oriented polymer should be perpendicular or tangential to the fibers to provide reinforcement in the transverse direction.

A number of recent reports[11–18] have appeared which indicate that the orientation of liquid crystalline monomers can be "frozen in" by polymerization. We reasoned that the polymerization of uniformly aligned monomers in the presence of fibers would result in a composite with an oriented matrix. A schematic which illustrates this concept is shown in Figure 2. The advantage of using liquid crystalline monomers vs. liquid crystalline polymers is that lower processing temperatures and pressures can be used due to the lower viscosities of the monomers. Another advantage is that transverse orientation of the polymer backbone should be easier to achieve. Transverse orientation is highly desirable because it would allow the oriented polymer to support loads in one direction and the fibers to support loads in a different direction. Bhama and Stupp[19] have briefly discussed the advantages of transverse orientation.

The key to the success of this approach is controlling the alignment of the liquid

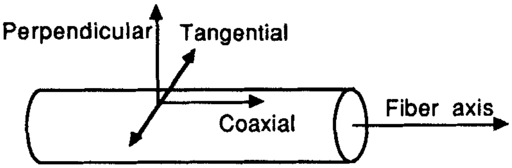

FIGURE 1 Principle axes of liquid crystal alignment on a fiber surface.

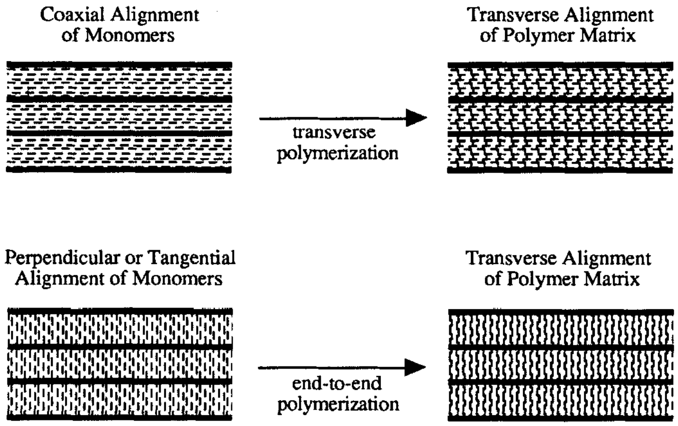

FIGURE 2 In situ polymerization of aligned liquid crystalline monomers to form an oriented polymer matrix.

crystalline monomers. If the monomers can be aligned coaxial to the fibers and polymerized so that the polymer backbones are perpendicular to the long axes of the molecules (by vinyl polymerization, for instance) then the polymer backbones will be oriented transverse to the fibers. Perpendicular or tangential alignment of the liquid crystalline monomers relative to the fiber axes followed by a polymerization which links the monomers together in an end-to-end fashion should also lead to an oriented matrix with transverse alignment. Bhama and Stupp[19] have demonstrated transverse alignment of polymer liquid crystals by grafting liquid crystal polyesters onto carbon fiber surfaces.

Since the success of this method depends upon the ease with which liquid crystals can be aligned on advanced fibers, we have begun to investigate the alignment of liquid crystals on fibers that are typically used in high performance composites. Our previous experiments dealt with the alignment behavior of a single nematic liquid crystal (MBBA) on four different carbon fibers. Encouraged by these results, the current study was designed to include a broader selection of liquid crystals and fibers. In this work, the surfaces of seven different fibers have been examined by scanning electron microscopy (SEM) and X-ray diffraction has been used to characterize the alignment of three different liquid crystals on these fibers. The results of these experiments are described below.

EXPERIMENTAL

The identities of the liquid crystals and fibers used in these experiments are shown in Table I. MBBA and 4′-pentyl-4-biphenylcarbonitrile (5CB) were selected because both were commercially available and both displayed a nematic phase at room temperature. The dielectric anisotropy $\Delta\varepsilon$ of MBBA is negative and the $\Delta\varepsilon$ of 5CB is positive[20] (materials with positive $\Delta\varepsilon$ tend to align parallel to an applied magnetic field; materials with negative $\Delta\varepsilon$ tend to align perpendicular). BN/75A was kindly supplied by Hallcrest Liquid Crystal Division, Glenview, Illinois. It is

TABLE I

Liquid crystal alignment on fibers

			Liquid Crystal Alignment		
Fiber Name	Fiber Type	Fiber Orientation	MBBA	5CB	BN/75A
E-130	Pitch-based carbon	High	∥	∥	∥
T–300	PAN-based carbon	High	∥	∥	∥
Kevlar 49	Aromatic Polyamide	High	∥	∥	∥
Spectra 1000	Polyethylene	High	∥	∥	∥
Spectra 1000 PT	Polyethylene, Plasma Teated	High	∥	∥	∥
FP	Alumina, Polycrystalline	Random	X	X	X
Nicalon	Silicon Carbide, Amorphous	None	X	X	X

MBBA and 5CB are nematic and BN/75A is a smectic A liquid crystal.

∥ : Liquid crystal was coaxial to the fiber.

X: Liquid crystal was randomly aligned. Occasionally, slight coaxial alignment was observed, but not reproducible. See text and Figures 11-12 for details.

a commercial liquid crystal mixture that exhibits a smectic A phase at room temperature. Carbon, organic and inorganic fibers were selected to provide a broad range of surface characteristics and orientations.

The alignment of the liquid crystals on the fibers was determined at room temperature by flat plate X-ray diffraction experiments on fiber tows (about 3000 individual filaments) which are swollen with an approximately equal weight of liquid crystal. MBBA and 5CB were applied to the fibers at room temperature; BN/75A was applied to the fibers from the isotropic melt. The experimental conditions have been described previously.[9]

RESULTS AND DISCUSSION

The alignment of the liquid crystals on the various fibers is shown in Table I and has been characterized as coaxial or random. The most important result of these experiments is that the alignment of all three liquid crystals was coaxial on the oriented fibers, but random on unoriented (polycrystalline or amorphous) fibers. The alignment occurred spontaneously upon application of the liquid crystal to the fiber without any particular surface treatment. The alignment was preserved when the swollen fiber was heated above the isotropization temperature of the liquid crystal and cooled back down to room temperature. The specific behavior of the liquid crystals on each side of the fibers is discussed below.

Carbon Fibers

We have previously[9] shown that MBBA aligns coaxial to E-130 and T-300 carbon fibers. In the present work, we have discovered that 5CB and BN/75A liquid crystals align coaxially on E-130 and T-300. The flat plate X-ray diffraction patterns obtained are very similar to our previous results. Visual examination of the diffraction patterns indicates that the degree of liquid crystal alignment is approximately the same for all of the liquid crystal and fiber types. The diffraction pattern of E-130/BN/75A shown in Figure 3 has two pairs of equatorial arcs. The outer pair corresponds to the ~3.4Å d-spacing characteristic of carbon graphitic (002) planes. The inner pair are due to the ~4.5Å intermolecular spacing of aligned BN/75A molecules. Note the typical meridional reflections at small angles that result from the alignment of the smectic A layer planes.

Our previous work[9] contained 5000X SEM photographs of the surfaces of E-130 and T-300 showing axial grooves and we speculated that the grooves may have caused the alignment of MBBA. A recent scanning tunneling microscopy (STM) investigation[21] of carbon fiber surfaces showed that atomic scale microgrooves were present on both pitch-based and PAN-based carbon fibers. Other workers[22-24] have employed small angle X-ray scattering (SAXS) to show that carbon fibers contain an oriented system of needle-shaped microvoids (~5 × 20 nm) which are roughly aligned with the graphitic basal planes. Although SAXS studies[23,24] of glycerin soaked carbon fibers indicate that the majority of these voids in the bulk of the fibers are inaccessible, the presence of oriented voids or microgrooves at the fiber surface probably influenced the alignment of the liquid crystals observed in this work.

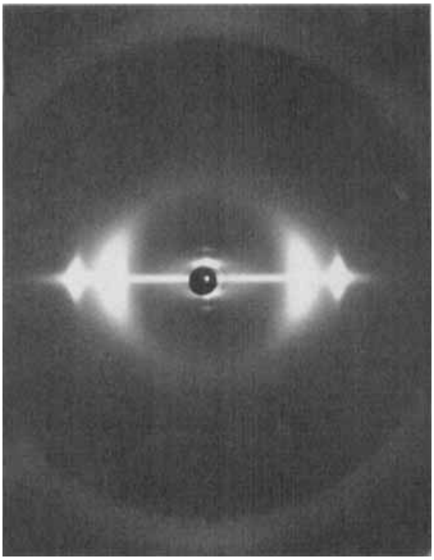

FIGURE 3 X-ray diffraction pattern of an E-130/BN/75A prepreg (fiber axis vertical).

Organic Fibers

Kevlar 49, Spectra 1000 and Spectra 1000 PT were the three organic fibers used in our X-ray diffraction studies of alignment. These three fiber types represent a range of surface characteristics. Kevlar 49 is the trade name given to a highly oriented aromatic polyamide made by Du Pont. The surface of Kevlar 49 is expected to be polar because of the presence of amide groups. Spectra 1000 and Spectra 1000 PT are the trade names given to one form of highly oriented, high molecular weight polyethylene sold by Allied Signal, Inc. Spectra 1000 PT is a plasma-treated form of Spectra 1000. This treatment probably increases the polarity of the rather non-polar hydrocarbon surface by the introduction of oxygen-containing functional groups.

Figure 4 shows a scanning electron microscope (SEM) photograph of the Spectra 1000 PT surface. Spectra 1000 PT has a rectangular cross section, with an irregular surface that contains occasional grooves. The surface of Spectra 1000 is similar to that of Spectra 1000 PT. Figures 5 and 6 show the X-ray diffraction patterns of Spectra 1000 and Spectra 1000/5CB, respectively. Although the X-ray diffraction pattern of Spectra 1000 contains reflections that overlap with the reflections of 5CB, Figure 6 clearly shows a pair of equatorial arcs that are not present in Figure 5. These arcs are due to 5CB that is aligned coaxially to the fibers. Visual examination of the diffraction patterns obtained for MBBA and BN/75A suggests that the degree of alignment exhibited by the three liquid crystals is very similar for both fibers, but this determination is less definitive than in the carbon fiber experiments because of the overlapping reflections. We are presently developing a computerized system to quantify the degree of alignment.

The presence of grooves on the surface of the Spectra 1000 fibers and the observation of uniform parallel liquid crystal alignment lends support to the idea that alignment is caused by the grooves. Preliminary SAXS experiments have indicated

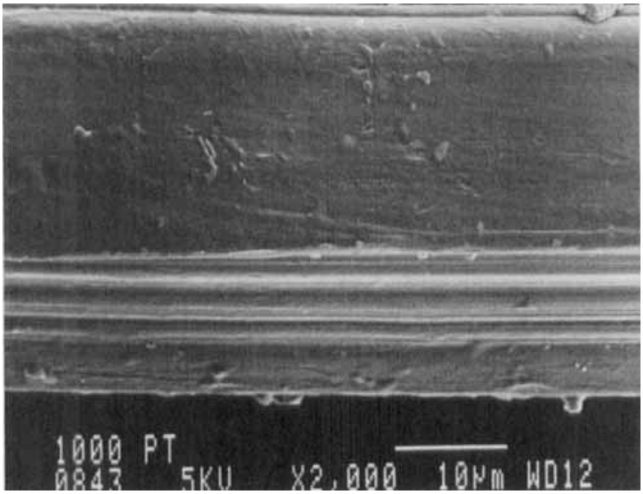

FIGURE 4 2000X SEM photo of a single spectra 1000 PT fiber.

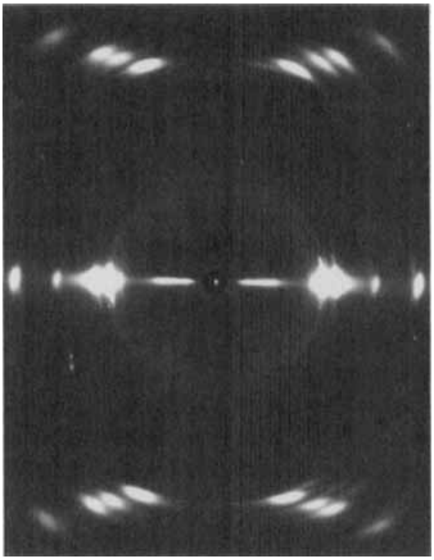

FIGURE 5 X-ray diffraction pattern of a spectra 1000 fiber tow (fiber axis vertical).

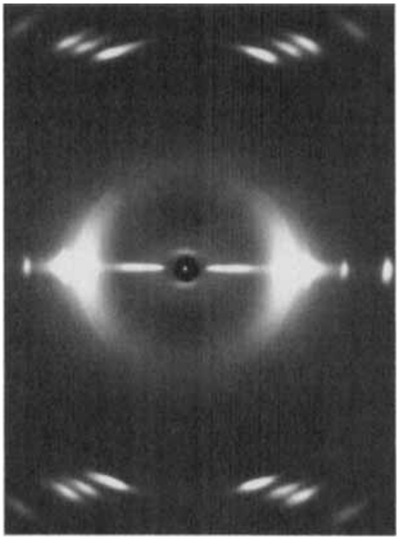

FIGURE 6 X-ray diffraction pattern of a spectra 1000/5CB prepreg (fiber axis vertical).

that the Spectra 1000 contains oriented microvoids or microgrooves that are similar to those observed for the carbon fibers, but less extensive. These features may also contribute to the alignment of the liquid crystals.

Figure 7 shows an SEM photograph of the surface of Kevlar 49. At these magnifications, it is apparent that Kevlar 49 has a round cross section with a rather smooth surface and no indication of grooves. The X-ray diffraction patterns of MBBA, 5CB and BN/75A on Kevlar 49 show a degree of coaxial alignment of the

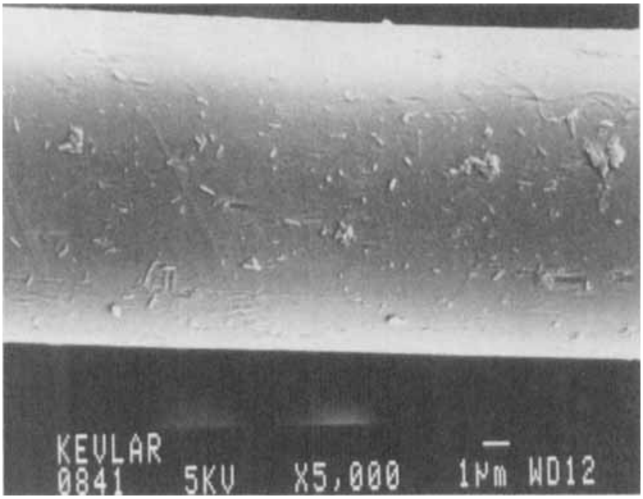

FIGURE 7 5000X SEM photo of a single Kevlar 49 fiber.

liquid crystals that is very similar to the coaxial alignment of 5CB shown in the Spectra 1000/5CB diffraction pattern (Figure 6). Although the Kevlar reflections overlap with the liquid crystal reflections, the evidence clearly shows that the liquid crystals are coaxially aligned. In the absence of grooves, the alignment mechanism of the liquid crystals is unclear, but may be related to the presence of oriented microgrooves. Dobb, Johnson and Saville[25] have shown that the surface region of Kevlar 49 contains a porous network of oriented microvoids which may act as microgrooves at the Kevlar 49 surface. These workers have employed transmission electron microscopy (TEM) and SAXS to show that Kevlar 49 has a skin-core morphology. The porous, 0.5–2.0 μm-thick skin contains needle shaped voids or fissures about 25 nm long and 5–10 nm wide that are oriented roughly parallel to the fiber axis. These features are not visible at 5000X by SEM. The core appears to be more compact and less porous. The void morphology of Kevlar 49 seems similar to the void structure of the carbon fibers discussed above.

Inorganic Fibers

Du Pont FP is a polycrystalline alumina fiber and Nicalon is an amorphous silicon carbide fiber. Figures 8 and 9 show the SEM photographs of FP and Nicalon, respectively. The FP surface is very granular, whereas the Nicalon surface is smooth and essentially featureless. There is no evidence of grooving on either surface. None of the liquid crystals aligned reproducibly on either Nicalon or FP. Figure 10 shows the X-ray diffraction pattern of Nicalon/MBBA. The outer halo is due to amorphous scattering by the Nicalon. The inner halo is due to unaligned MBBA. Figure 11 shows the X-ray diffraction pattern of FP/BN/75A. The sharp rings in Figure 11 are due to the randomly oriented polycrystalline alumina (Al_2O_3). The slight arcing of the inner halo shows that the BN/75A is partially aligned. When the FP/BN/75A was heated to isotropization and cooled, the alignment disappeared as shown in Figure 12.

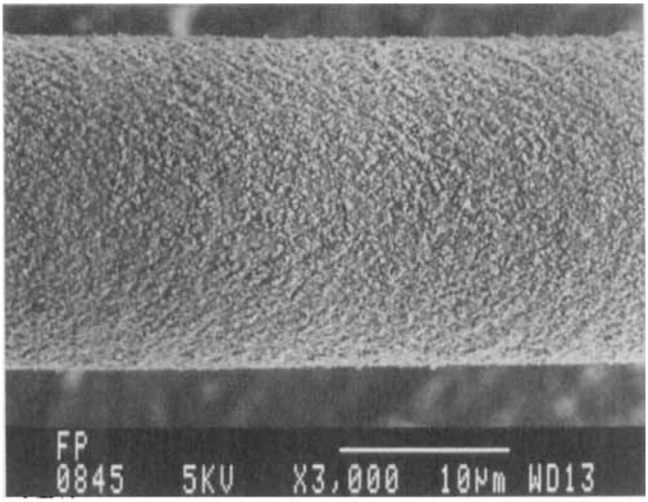

FIGURE 8 3000X SEM photo of a single FP fiber.

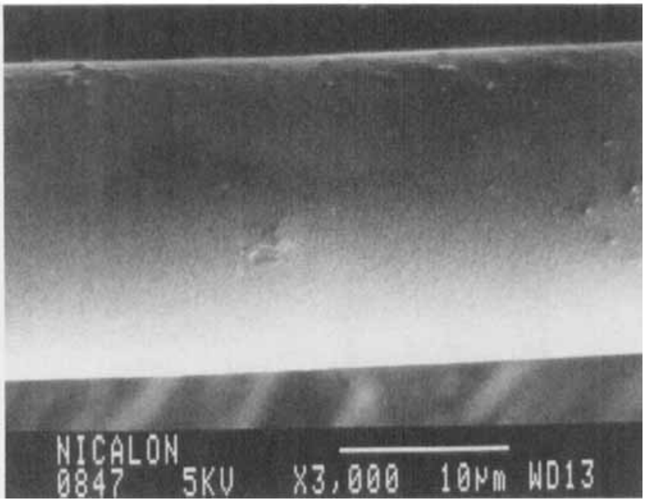

FIGURE 9 3000X SEM photo of a single Nicalon fiber.

Although all three liquid crystals were generally unaligned on FP and Nicalon, alignment similar to that seen in Figure 11 was occasionally observed during the course of these experiments. Isotropization of the liquid crystal followed by cooling to room temperature generally eliminated the alignment. This is the same sort of transient alignment that is often observed when glass capillaries are used to contain liquid crystals for X-ray diffraction. It is well known[5] that reproducible alignment is difficult to obtain on untreated inorganic and oxide surfaces and our results are in accord with these previous observations. Previous X-ray scattering studies of Nicalon have shown[26] that the fibers contain unoriented globular nanopores. Preliminary SAXS studies on Nicalon and FP have been performed in our laboratory

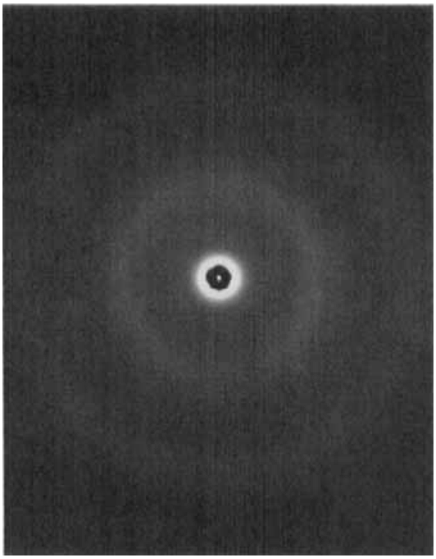

FIGURE 10 X-ray diffraction pattern of a Nicalon/MBBA prepreg (fiber axis vertical).

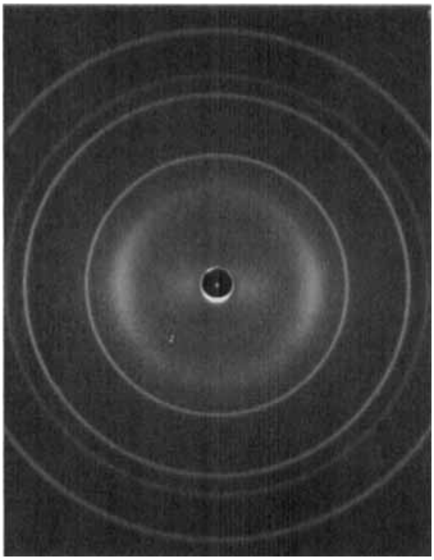

FIGURE 11 X-ray diffraction pattern of an FP/BN/75A prepreg (fiber axis vertical).

which confirm these results and show that neither fiber contains an oriented microvoid structure. The observation that liquid crystals do not align on Nicalon or FP supports the idea that the alignment observed on the oriented fibers was caused by oriented surface features.

Magnetic fields, flow, and surface effects are the known methods of orienting liquid crystals. In these experiments, MBBA and 5CB were always aligned in the

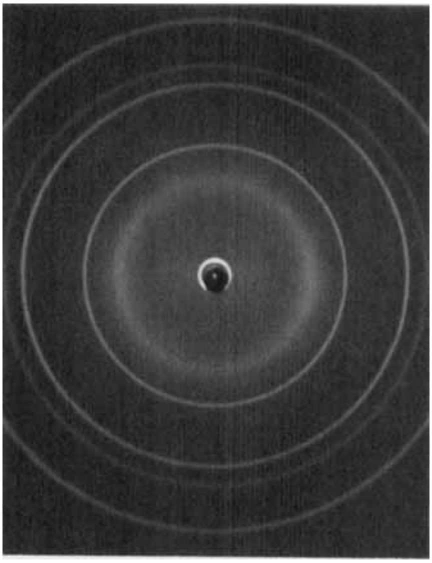

FIGURE 12 X-ray diffraction pattern of an FP/FN/75A prepreg (fiber axis vertical) at room temperature after BN/75A isotropization.

same direction and no known local magnetic fields were present, so it is very unlikely that magnetic fields caused the alignment. The dielectric anisotropy values of MBBA and 5CB are opposite in sign, so the two liquid crystals would have aligned differently if magnetic fields had been the cause of alignment. It is also unlikely that flow caused by wicking of the liquid crystals along the fibers was the primary cause of alignment, since wicking also occurred on FP and Nicalon and did not result in reproducible alignment. Wicking could have been a contributing factor, however, since occasional slight orientation on FP and Nicalon was observed. Therefore, it seems most likely that the primary cause of alignment was surface effects.

The results of these experiments show that there is a strong correlation between fiber orientation and liquid crystal alignment. All three of the liquid crystals used in this study aligned coaxially on oriented fibers and none of them aligned reproducibly on unoriented fibers. The high degree of order which presumably exists in the liquid crystals at the surface of the oriented fibers is largely retained in the bulk of the liquid crystal between fibers, although the degree of order at the surface may be higher than the bulk order (see below). The average distance between fibers is on the order of 10 μm, which is comparable to the spacing between the front and rear plates (6–15 μm) in a typical liquid crystal display cell.[27] Surface treatments which result in grooving are typically used on the plates in a display cell to induce bulk liquid crystal order, and a similar effect of the fiber surfaces on liquid crystal alignment seems likely in these experiments.

We hypothesize that the coaxial alignment of the liquid crystals used in this work resulted from the influence of (1) oriented microscopic grooves and/or (2) oriented nanoscale surface features such as polymer crystallites or carbon fiber basal plane edges. Theoretical and experimental work have indicated that liquid crystals align uniformly parallel to surface grooves. For a discussion of the influence of groove depth and spacing on liquid crystal alignment, see Cognard.[5] All of the oriented fibers except Kevlar have surface grooves visible at 5000X. In the case of Kevlar, the presence of large scale surface grooves was not observed, but the presence of small scale grooves was inferred from the work of Dobb, Johnson and Saville.[25] As noted previously, nanoscale grooves may also be present on carbon fibers and Spectra 1000.

The idea that nanoscale surface features can influence bulk orientation is supported by recent experiments[28,29] involving the alignment of liquid crystals and other materials on oriented films of poly(tetrafluoroethylene) (PTFE). The alignment of the liquid crystals was shown to be strongly dependent on the molecular orientation of the PTFE substrate. A recent STM study[30] has also shown that the alignment of organic monolayers on graphite is very sensitive to the orientation of nanoscale surface features. The relative influence of oriented surface grooves visible at 5000X and oriented nanoscale surface features (not visible at 5000X) on the alignment of liquid crystals is unknown. The difference between grooves and oriented nanoscale surface features may only be a difference in scale, but further experiments are necessary to characterize the correlation between the size of the surface feature and the degree of liquid crystal alignment.

We find it curious that the degree of liquid crystalline alignment seems relatively equal on all of the oriented fibers, despite the seemingly wide range of surface feature orientations and morphologies that are present. We speculate that the degree of liquid crystal alignment at the fiber surface may be strongly correlated with the surface orientation, but that this high degree of order is not completely transmitted to the bulk of the liquid crystal. X-ray diffraction measurements of the bulk order thus give similar results for all of the oriented fibers because the degree of bulk alignment is not strongly correlated with the degree of surface orientation. It seems logical to assume that the ability of the fiber surface to induce liquid crystal alignment fades as the distance from the fiber increases.

In this work, we have discovered that certain nematic and smectic A liquid crystals become coaxially aligned on several technologically important carbon and organic fibers. None of the liquid crystals aligned perpendicular or tangential to the fiber surface. For practical applications involving composite materials, it would also be desirable to achieve perpendicular or tangential alignment. The development of liquid crystal display technology has resulted in a number of methods for achieving perpendicular alignment. For instance, treatment of the surface with a surfactant or dissolving a surfactant in the liquid crystal is often effective.[5] The desirability of perpendicular or tangential alignment is illustrated in Figure 2, which shows two hypothetical methods for preparing composites with matrices that are oriented transverse to the fibers. Since main chain liquid crystal polymers have much better mechanical properties than side chain liquid crystal polymers, the end-to-end polymerization of monomer liquid crystals that are aligned perpendicular or tangential to the fibers will probably produce a better composite matrix. Unfortunately, many end-to-end polymerizations proceed by a condensation reaction that produces a low molecular weight by-product that could be difficult to remove from the composite. The best liquid crystal monomers for the end-to-end polymerization method would probably contain end groups such as epoxy/amine that react without evolving volatiles. Chemical reactions between the liquid crystals and surface may also influence alignment. Perpendicular alignment of polyester liquid crystals was shown to occur spontaneously when the polymer was grafted to the fiber surface.[19]

CONCLUSION

We have discovered that two nematic liquid crystals (MBBA and 5CB) and one smectic A liquid crystal (BN/75A) became coaxially aligned on several technologically important fibers when the fibers were swelled with an approximately equal weight of the liquid crystal. The alignment was spontaneous and did not change after a heat/cool cycle which isotropized the liquid crystals. Reproducible coaxial alignment was only observed on oriented fibers and random alignment was observed on unoriented polycrystalline and amorphous fibers. SEM was used to show that surface grooves were present at 2000–5000X on all of the oriented fibers except Kevlar 49. Since surface grooves are known to induce uniform parallel alignment of liquid crystals, it seems likely that they contributed to the alignment of the liquid crystals in this work. In the case of Kevlar 49, the alignment was apparently caused by oriented small scale features that are not visible at 5000X. Recent experiments[28,29] have shown that liquid crystals can be aligned by oriented PTFE films, so it seems likely that oriented nanoscale features on the carbon, Spectra 1000 and Kevlar 49 fiber surfaces such as polymer crystallites and the edges of carbon fiber basal planes also contributed to the alignment of the liquid crystals observed in this work.

In spite of the wide differences in surface morphology between the various oriented fibers, the degree of alignment of the liquid crystals on each of the oriented fibers was approximately equal. We speculate that the degree of liquid crystal orientation is closely correlated to the degree of surface feature orientation at the fiber surface, but that this correlation fades as the distance from the fiber increases.

The facile alignment of several liquid crystals on oriented fibers suggests that composites with oriented matrices can be prepared by the in situ (in the presence of fibers) polymerization of oriented liquid crystalline monomers. Oriented polymer matrices should substantially increase the mechanical properties of the resulting composite materials, particularly if transverse alignment of the polymer backbone can be achieved. Transverse alignment can result from parallel, tangential or perpendicular alignment of the liquid crystalline monomers, depending on the method used to polymerize them. The most promising route appears to be the end-to-end polymerization (preferably without condensation by-products) of liquid crystalline monomers that are aligned perpendicular or tangential to the fibers.

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