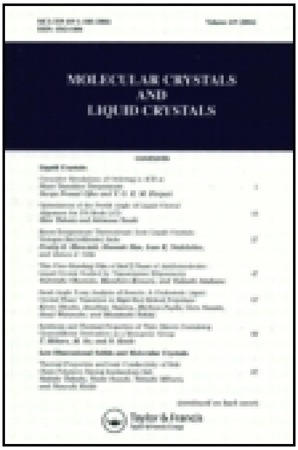

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Characterization of Liquid Crystal Alignment on Carbon and Organic Fibers by Quantitative X-ray Diffraction

Joseph J. Mallon [a] & Paul M. Adams [b]

[a] American Cyanamid Co., Chemical Research Division, Stamford, CT

[b] The Aerospace Corporation, 2350 E. El Segundo Blvd., El Segundo, CA, 90245

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Characterization of Liquid Crystal Alignment on Carbon and Organic Fibers by Quantitative X-ray Diffraction

JOSEPH J. MALLON† and PAUL M. ADAMS
The Aerospace Corporation, 2350 E. El Segundo Blvd., El Segundo, CA 90245

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We have previously reported that the degree of 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 four different carbon fibers was approximately equal. The uniform alignment of the liquid crystals was coaxial to the fibers and occurred spontaneously upon application of the liquid crystals to the fibers; no special surface treatments were required. In the current work, we have quantified the degree of liquid crystal alignment by developing a method to retrieve peak intensity values from flat film X-ray diffraction patterns. This method uses readily available image analysis technology to extract, store, manipulate and analyze the information derived from these patterns. The azimuthal full width at half maximum (FWHM, a measure of the degree of alignment) of each of the aligned liquid crystals on T-300, T-50, P-55 and E-130 carbon fibers and the FWHM of the fibers themselves have been determined by this method. At room temperature, the FWHM values for MBBA, 5CB and BN/75A, were 58° ± 3°, 56° ± 4° and 45° ± 5°, respectively, regardless of the degree of preferred orientation of the fiber substrate. The degree of liquid crystal alignment was slightly higher on PAN-based fibers than on pitch-based fibers. These measurements support our previous contention that the degree of liquid crystal alignment is relatively insensitive to the degree of preferred orientation in the fibers provided the orientation exists. The same series of liquid crystals showed a similar degree of coaxial alignment on oriented polyethylene and poly(tetrafluoroethylene) fibers.

Keywords: liquid crystal, 4-methoxybenzylidene-4′-n-butylaniline (MBBA), 4′-pentyl-4-biphenylcarbonitrile (5CB), 4-ethoxybenzylidene-4′-n-butylaniline (EBBA), carbon fibers, polyethylene, poly(tetrafluoroethylene), nematic, smectic, alignment, X-ray diffraction.

INTRODUCTION

Previous work[1-3] in our laboratory showed that certain nematic and smectic liquid crystals became uniformly aligned when placed in contact with carbon and organic fibers that have a crystalline preferred orientation, but remained unaligned on unoriented inorganic fibers. The bulk 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 commercial fibers was characterized by flat film X-ray diffraction. We concluded that the uniform alignment of the liquid crystals was probably caused

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†Present address: American Cyanamid Co., Chemical Research Division, Stamford, CT.

by grooves, microgrooves, and/or oriented features such as polymer crystallites on the surfaces of the oriented fibers. The lack of uniform alignment on the unoriented fibers was attributed to the lack of these oriented surface features. Our conclusions were supported by the well known[4] tendency of liquid crystals to align on grooved surfaces. One puzzling aspect of our previous work concerned the alignment of MBBA on a series of four carbon fibers with different surface structures and different degrees of preferred orientation. In spite of the differences in substrate morphology, the overall degree of alignment of the MBBA seemed to be essentially the same on all four of the carbon fibers. Our assessment of the degree of MBBA alignment, however, was based on qualitative comparisons of the flat film X-ray diffraction patterns.

In an effort to quantify the degree of alignment, we have developed a technique utilizing readily available image analysis technology to extract, store, manipulate and analyze information contained in flat film X-ray diffraction patterns. Our experimental work was extended by obtaining X-ray diffraction patterns for liquid crystals 5CB and BN/75A on the same series of four carbon fibers used for the MBBA experiments. In addition, we have also begun studies of the alignment of these liquid crystals on oriented polyethylene (PE) and poly(tetrafluoroethylene) (PTFE) fibers. In the report that follows, a detailed description of the image analysis technique is presented, followed by the results of the liquid crystal alignment experiments.

EXPERIMENTAL

Flat film X-ray diffraction patterns were obtained at room temperature using both bare fiber samples and fiber samples that had been swelled with an approximately equal weight of either MBBA, 5CB or BN/75A; the sample preparation and X-ray diffraction conditions for the swollen fiber samples have been described previously.[1-3] Exposure times for the bare fibers were adjusted to produce an optical density (see below) of less than 2.0 for the graphitic (002) reflection, and ranged from five minutes to two hours.

Quantitative measurements of the degree of preferred orientation, which is a function of the full width at half maximum (FWHM) of the azimuthal intensity profile for the dominant crystalline fiber and liquid crystal reflections, were obtained from the X-ray films by digitizing both the images and a Kodak photographic step tablet (No. 2). This was accomplished by backlighting the patterns and step tablet with a light box in a darkened room in order to prevent reflected light from interfering with the measurements. The optical system which consisted of a Pulnix TM 745 charge coupled device (CCD) camera equipped with a Nikon 50 mm macro lens was interfaced by means of an 8-bit Data Translation DT2255-60Hz frame grabber board to a Macintosh II FX computer, which operated with a National Institute of Health (NIH) Image version 1.22 image analysis software package. The CCD camera was used in a manual gain mode with the gain adjusted so that the optical density of any region on a film was not influenced by the overall density of the complete image. Each film and the step tablet were digitized (without moving the film), with frame averaging (16 frames) to minimize noise, using two shutter speeds (1/60, 1/250 sec.) for the CCD in order to extend the limited (0-255) grayscale range over a greater spread of optical density. These digitized images (TIFF files) of the patterns were then transferred by an Ethernet link to a VAX 4000 computer for data processing using Interactive Data Language (IDL).

The following procedure was used for constructing azimuthal intensity scans from the digitized images:

1. Calibration curves of optical density vs. grayscale were constructed from the step tablet for the two shutter speed settings.
2. The pixel location (x, y coordinates) of the direct beam was determined using the NIH Image software (in particular the zoom feature). Similarly, the pixel locations for the peaks of the reflections of interest were determined. From this information the reflection radius could be determined.
3. These pixel values were input into an IDL computer program which then located pixels in the image which had the appropriate radius (to within 0.5 pixels) values from the direct beam. This search process was simplified by only evaluating pixels within a narrow abscissa window for each ordinate. The position of the window was determined by the known radius and the given ordinate. When a pixel met these criteria, its net optical density was determined from the two TIFF files recorded at different shutter speeds, the optical density vs. grayscale calibration curves, and the optical density of the background. The net optical density and theta (polar coordinates, not Bragg angle) value were then stored in an array. At the conclusion of the pixel selection the arrays from each side of the film were sorted by theta and the intensity normalized, thereby providing intensity as a function of theta (azimuthal intensity profile).
4. The FWHM of the azimuthal intensity profile could be used directly as a measure of the preferred orientation. However, for the most highly crystalline and oriented fibers (E-130 and Spectra 1000) the peak of the azimuthal profile had a contribution from Bremsstrahlung and small angle scattering. For this reason, and to minimize the effect of noise, the azimuthal intensity profiles were fit with a Gaussian function. In the case of the E-130 and Spectra fibers, the Gaussian profile was determined by omitting the data at the peak (± 3–$5°$) in the fit, thereby eliminating the effects from the fibers.
5. The entire image analysis procedure was repeated on each of the flat film X-ray diffraction patterns to establish the average alignment and standard deviation. At least two and as many as four patterns were obtained for each carbon fiber/liquid crystal combination; the alignment values were thus the average of at least four and as many as eight data points. Some of the organic fiber/liquid crystal data were based on the average of two image analyses on a single flat film pattern.

RESULTS AND DISCUSSION

We have previously reported that MBBA, 5CB and BN/75A aligned coaxial to carbon fibers E-130, P-55, T-50 and T-300.[3] By applying the image analysis technique described above to the flat film X-ray diffraction patterns, the full width at half maximum (FWHM) of each of the main liquid crystal and carbon fiber diffraction peaks has been measured. FWHM values can range from 0° to 90° and are inversely proportional to the degree of orientation. Figure 1 shows the X-ray

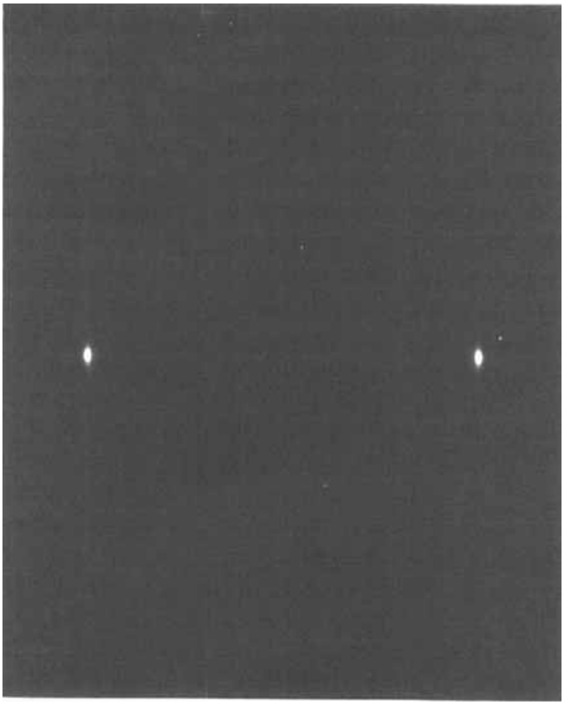

FIGURE 1 X-ray diffraction pattern of an E-130 fiber tow (fiber axis vertical).

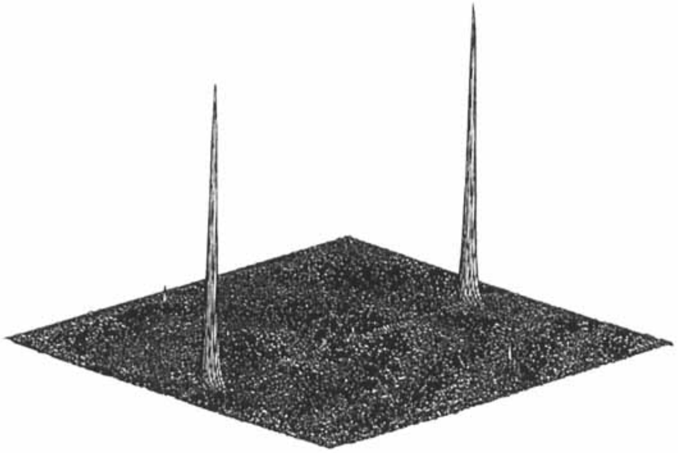

FIGURE 2 Pseudo three-dimensional plot derived from the X-ray diffraction pattern shown in Figure 1.

diffraction pattern of an E-130 fiber tow; Figure 2 shows the pseudo three dimensional plot derived from that pattern by the image analysis. In Figure 3, the normalized intensity of the graphitic (002) reflection has been plotted as a function of azimuthal angle. The FWHM value for E130 was derived from the Gaussian fit of this plot, which represents a constant radius circular slice of Figure 2. An analogous series of plots are shown in Figures 4 through 6 for E-130/5CB (an E-130 fiber bundle swollen with 5CB). The E-130 peaks have been truncated in the pseudo-three dimensional plot shown in Figure 5 to emphasize the alignment details of the 5CB.

The FWHM values for each of the carbon and organic fibers and liquid crystals are given in Table I, along with the 2σ standard deviation of the data. We define an alignment function $F = 1 - \mathrm{FWHM}/90$ to normalize the FWHM data; when $F = 1$ the sample is perfectly oriented and when $F = 0$ the sample is randomly oriented. The corresponding F values for each of the FWHM values are given in Table I. Figure 7 shows a plot of F (liquid crystals) vs. F (carbon fibers) with 2σ error bars. This plot shows that the alignment of the liquid crystals is relatively insensitive to the orientation of the fiber substrate. As expected, the degree of

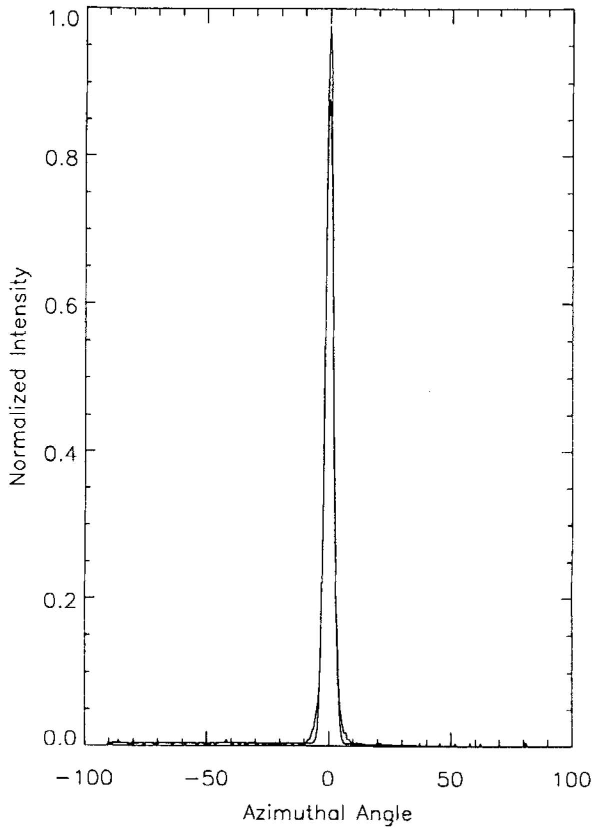

FIGURE 3 Intensity of graphitic (002) reflection as a function of azimuthal angle for E-130 fibers (constant radius circular slice of Figure 2).

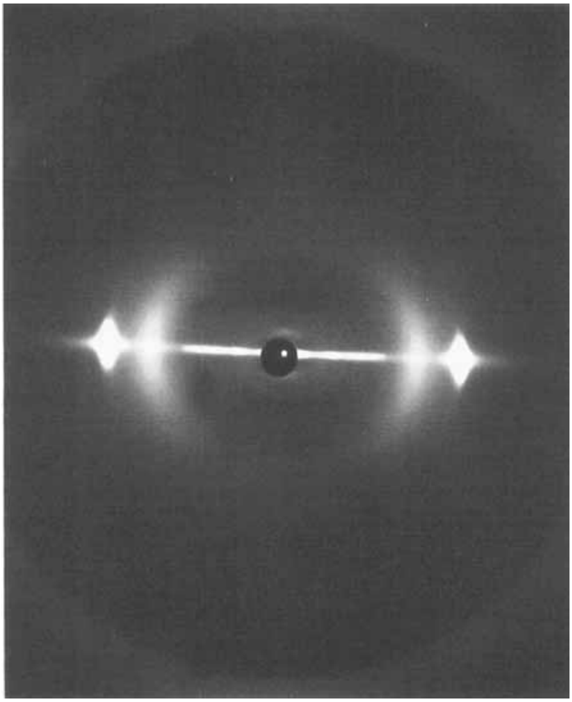

FIGURE 4 X-ray diffraction pattern of an E-130/5CB prepreg tow (fiber axis vertical).

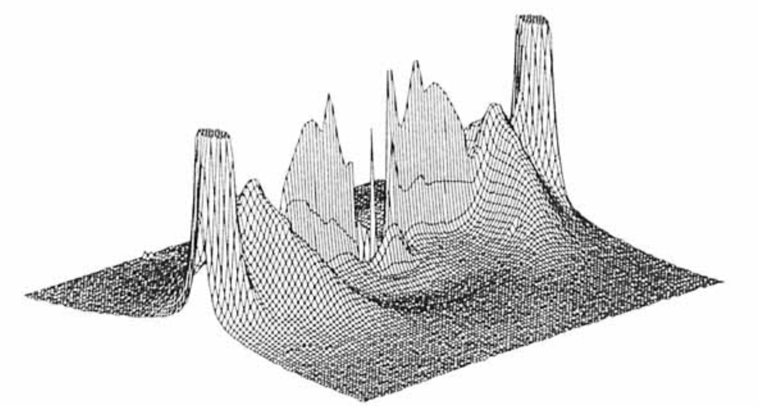

FIGURE 5 Pseudo three-dimensional plot derived from the X-ray diffraction pattern shown in Figure 4 (E-130 peaks truncated to show detail).

alignment of the two nematic liquid crystals was nearly the same, whereas the smectic liquid crystal BN/75A was more highly aligned. These results demonstrate that there is no correlation between the *degree* of bulk fiber preferred orientation and the *degree* of bulk liquid crystal alignment. However, we have shown previously[1–3] that there is a strong correlation between the *presence* of bulk fiber preferred orientation and *presence* of liquid crystal alignment.

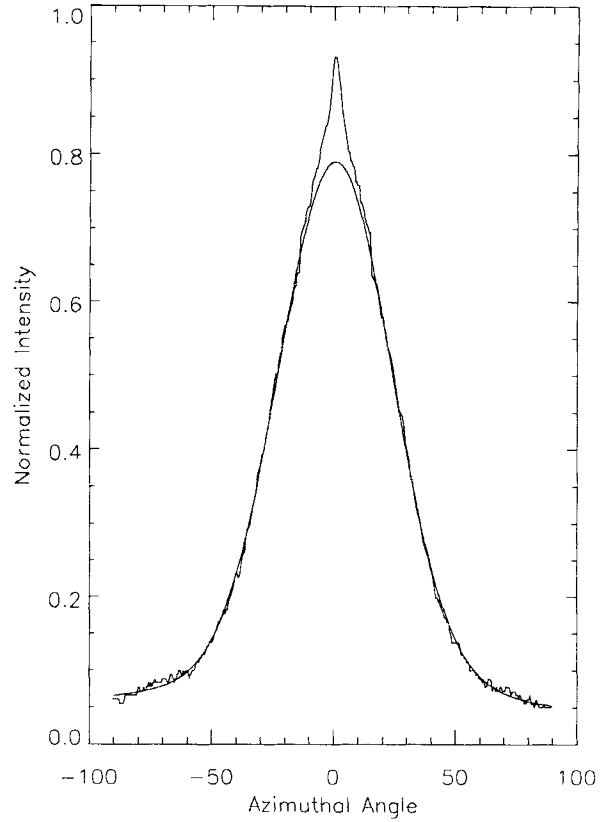

FIGURE 6 Intensity of 5CB liquid crystal reflection as a function of azimuthal angle for E-130/5CB (constant radius circular slice of Figure 5).

For each liquid crystal, there is a "step" in the middle of the *F* (liquid crystal) vs. *F* (carbon fiber) plot (Figure 7) that appears to be due to the type of carbon fiber. For each liquid crystal, the *F* values on the left side of Figure 7 were due to alignment on PAN-based carbon fibers (T-300 and T-50) and the *F* values on the right side of the plot were due to alignment on pitch-based carbon fibers (P-55 and E-130).[5] Although the step is not large, it is present for all three of the liquid crystals and indicates a small but significant decrease in alignment on going from the PAN-based fibers to the pitch-based fibers. This alignment decrease may be due to the differences in surface morphology between these two types of fibers.[6] However, due to the level of uncertainty in the data, we are hesitant to attach a great deal of significance to this "step" until other fibers and fiber/liquid crystal combinations have been examined.

Table I also contains the FWHM and *F* values for the three liquid crystals on oriented polyethylene (PE) and poly(tetrafluoroethylene) (PTFE) fibers, as well as the corresponding values for the fibers themselves. The X-ray diffraction patterns of the liquid crystals and the organic fibers overlapped to some extent, complicating efforts to quantify the alignment. In fact, the Kevlar 49/liquid crystal X-ray diffraction patterns reported previously[2] could not be analyzed by the image analysis

TABLE I

FWHM and *F* values for fiber tows and liquid crystals on fiber tows

	Fiber	MBBA	5CB	BN/75A
E-130 (Carbon, pitch-based)				
FWHM (2σ)	4.4 (0.2)	60.5 (4.1)	55.4 (3.8)	47.7 (1.8)
F (2σ)	0.95 (<0.01)	0.33 (0.05)	0.38 (0.04)	0.47 (0.02)
P-55 (Carbon, pitch-based)				
FWHM (2σ)	14.9 (0.2)	60.3 (2.9)	59.3 (3.7)	49.5 (2.0)
F (2σ)	0.83 (<0.01)	0.33 (0.03)	0.34 (0.04)	0.45 (0.02)
T-50 (Carbon, PAN-based)				
FWHM (2σ)	17.0 (0.2)	57.1 (1.2)	52.4 (2.0)	41.0 (2.2)
F (2σ)	0.81 (<0.01)	0.37 (0.01)	0.42 (0.02)	0.54 (0.02)
T-300 (Carbon, PAN-based)				
FWHM (2σ)	34.2 (0.4)	55.3 (2.1)	53.2 (2.3)	44.7 (3.5)
F (2σ)	0.62 (<0.01)	0.39 (0.02)	0.41 (0.03)	0.50 (0.04)
Spectra 1000 (PE)				
FWHM (2σ)	5.3 (0.1)	55.3 (1.4)	52.8 (5.3)	44.8 (2.8)
F (2σ)	0.94 (<0.01)	0.39 (0.02)	0.41 (0.06)	0.50 (0.03)
Spectra 1000 PT (PE, Plasma-treated)				
FWHM (2σ)	5.3 (0.1)	58.6 (1.7)	58.3 (7.7)	50.8 (4.5)
F (2σ)	0.94 (<0.01)	0.35 (0.02)	0.35 (0.09)	0.44 (0.05)
Teflon (PTFE)				
FWHM (2σ)	14.9 (0.4)	50.1 (3.5)	53.5 (3.6)	49.1 (4.7)
F (2σ)	0.83 (<0.01)	0.44 (0.04)	0.41 (0.04)	0.45 (0.05)

techniques described above because of severe peak overlap. Because of these difficulties, fewer experiments were performed on these systems and the corresponding levels of uncertainty tended to be higher (2σ values shown in Table I).

In spite of these difficulties, however, the degree of liquid crystal alignment on the organic fibers clearly showed the same general trends observed for the carbon fibers: the smectic liquid crystals were more aligned than the nematic liquid crystals, and the overall degree of alignment was relatively insensitive to the degree of substrate preferred orientation. The coaxial alignment on PTFE is especially interesting because liquid crystals usually align perpendicular to low energy surfaces such as PTFE.[4] Plasma treatment of the low energy PE surface (Spectra 1000 vs. Spectra 1000PT) did not appear to cause a significantly different degree of alignment for any of the three liquid crystals.

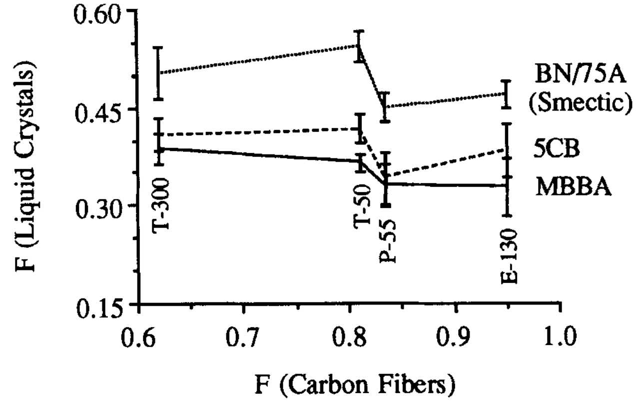

FIGURE 7 Degree of liquid crystal alignment [*F* (liquid crystals)] as a function of the degree of carbon fiber alignment [*F* (carbon fibers)] with 2σ error bars. Greater *F* means greater alignment.

In a preliminary series of experiments, we have found that the alignment of the liquid crystals is strongly dependent on temperature and that the uniform coaxial alignment becomes random at a temperature below the isotropization temperature. These experiments have been conducted with both MBBA and 4-ethoxybenzylidene-4′-*n*-butylaniline (EBBA) on E-130 fibers and were conducted by obtaining diffraction patterns at various sample temperatures. In both cases, the degree of MBBA and EBBA alignment decreased as the temperature increased, and the uniform coaxial alignment became random before isotropization. The transition from aligned liquid crystal to unaligned liquid crystal was not detected by differential scanning calorimetry (DSC). The position of the transition was difficult to reproduce; for EBBA (T_i = 78°C) the aligned-to-unaligned transition ranged from 45°C to 65°C. These results have important implications for the development of composites with oriented matrices by the in situ polymerization of aligned liquid crystalline monomers.[1-3] If the monomers do not remain aligned at the cure temperature, then an oriented matrix is not expected to form. Future experiments are needed to establish the temperature dependence of the alignment phenomenon.

CONCLUSION

We have previously reported that the degree of bulk MBBA alignment on a series of four carbon fibers was relatively insensitive to the degree of bulk fiber substrate preferred orientation. This assertion was based on qualitative comparisons of flat film X-ray diffraction patterns. In the present work, we have obtained flat film X-ray diffraction patterns of two other liquid crystals, MBBA and BN/75A, on the same series of carbon fibers and we have developed a relatively low cost image analysis method to quantify the flat film data. These experiments have extended our earlier results by confirming that the degree of liquid crystal alignment is relatively insensitive to the degree of substrate fiber orientation for both nematic and smectic liquid crystals. As expected, the smectic A liquid crystal (BN/75A) was more highly aligned than the two nematic liquid crystals (MBBA and 5CB). These experiments also revealed a small but significant alignment decrease on going from PAN-based to pitch-based carbon fibers. The statistical confidence of this observation is not high, however (approximately 1σ level, or 68%), so further discussion of this observation may be premature.

The image analysis technique was also applied to organic fiber/liquid crystal diffraction patterns. These analyses were complicated by some overlap between the fiber and liquid crystal reflections. In spite of these difficulties, data was obtained which showed that the degree of smectic liquid crystal alignment was higher than the degree of nematic liquid crystal alignment. The overall degree of liquid crystal alignment on the organic fibers was similar to that observed on the carbon fibers and was also relatively insensitive to the degree of preferred orientation in the fiber.

Some preliminary X-ray diffraction experiments were conducted to determine the temperature dependence of the liquid crystal alignment on carbon fibers. We found that an aligned-to-unaligned transition took place well below the isotropization temperature of the liquid crystal. Further study of this phenomenon is needed before composites with oriented matrices can be prepared by the in situ polymerization of aligned liquid crystalline monomers.

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6. Reference 1 discusses the differences in surface morphology between pitch- and PAN-based carbon fibers and contains SEM photos of each of the fibers used in the current study.