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THERMALLY INDUCED REORGANIZATION IN LCP FIBERS
Molecular origin of mechanical strength*

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The molecular reorganization occurring in liquid crystalline polymer fiber during heat treatment is of great interest for many commercial reasons. Using thermal analysis techniques, WAXS and real time temperature dependent synchrotron SAXS, the structure and morphology of commercial LCP (liquid crystalline polymer), Vectran®, HBA/HNA (*p*-hydroxybenzoic acid/6-hydroxy-2-naphthoic acid), and its variant polymer fiber COTBP, HBA/HNA/BP/TA (BP-benzophenone, TA-terephthalic acid), have been examined. Both fibers have the typical liquid crystalline polymer structure, i.e., highly aligned with aperiodic sequencing along the fiber axis. There is a three-fold increase in strength in both fibers with heat treatment; however, the modulus is observed to increase significantly in COTBP but not in Vectran®.

This paper reports on the changes and the differences on the structural and morphological behavior for both the as-spun and heat-treated LCP fibers. We propose an 'oriented entanglement' model to describe the differences between the two polymer fibers.

Keywords: *COTBP, heat treatment, LCP fiber, mechanical elements, oriented entanglements, tensile properties, Vectran®*

Introduction

Liquid crystal polymer fibers (LCP) are of high commercial interest because of high tensile properties that can be achieved. Vectran® is a wholly aromatic polyester that behaves as a thermotropic LCP. It is commercially melt spun into highly oriented fibers that exhibit tensile properties that are much higher than those that are observed in conventional melt spun fiber, for example, polyethylene terephthalate (PET) or polyethylene (PE). Vectran® yarn is marketed as having specific strength that approaches 10 times that of titanium, stainless steel and aluminum [1]. These high properties make it a material suitable for use in the fabrication of the protective crash bags in the Spirit, Opportunity and Pathfinder missions to Mars [2].

It is well known that some of the necessary conditions to achieve high modulus fibers include high molecular orientation, high ordered lateral packing and low concentration of axial defects. The highest modulus obtainable is achieved with highly oriented chains in non-crystalline domains [3, 4]. The development of tensile strength requires that there be some mechanical elements that connect adjacent chains in a manner that prevents them from slipping past each other under tensile load. For PET fiber, the careful manipulation of the thermal program and spinline stress results in the development of crystallinity that accomplishes this mechanical connectivity. For melt spun fibers from wholly aromatic polyester LCP, a heat treatment step is required to develop the high tensile properties. The nature of the mechanical connectivity that develops during that heat treatment is not well understood at the molecular scale. An 'aggregate model' has been proposed without any clear specification what the molecular nature of the 'aggregates' would be [5]. Another historically recurring notion is that the development of high properties during heat treatment is associated with a thermally induced solid state increase in molecular mass, without the specification of any specific, discrete mechanical elements in the internal structure of the fiber at the molecular level [6, 7].

In commercial production, the heat treatment step is costly and time consuming. Historically, optimal heat treatment programs have been developed in the plants by empirically varying process conditions and maximizing the resulting properties. Understanding the molecular mechanism of property

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development has the potential to provide a rational framework for process improvement. Further, it opens the possibility for radically different modes of processing based on facilitating the development of the specific mechanical elements required for property development.

In this work, we examined the as-spun and heat-treated state of two wholly aromatic LCP fibers, a co-polymer of *p*-hydroxybenzoic acid/6-hydroxy-2-naphthoic acid (HBA/HNA), commercially sold as Vectran®, and a composition consisting of HBA/HNA/BP/TA (BP-benzophenone, TA-terephthalic acid). This experimental composition is designated COTBP. Using WAXS and synchrotron SAXS techniques as well as thermal analytical methods including DSC, DMA, TMA and TSC, the evolution of internal structure was examined with a focus on identifying specific molecular scale mechanical elements that could account for an increase in tensile strength.

Experimental

Samples

Fiber samples were obtained from commercial sources (Celanese Corporation). Vectran® fiber has both HBA/HNA (73/27, HBA=4-hydroxybenzoic acid, HNA=2-hydroxy-6-naphthoic acid). COTBP is a variant of Vectran® with two additional monomers, HBA/HNA/BP/TA (BP-benzophenone, TA-terephthalic acid). Both as-spun and heat-treated fibers of Vectran® and COTBP were examined in this investigation. Results are reported for fibers heat treated using commercially established protocols. Briefly stated, for Vectran® the heat treatment program is 1 h at 230°C followed by 16 h at 270°C. For COTBP the heat treatment program is 8 h at 300°C. This difference in heat treatment protocols was found to be necessary to maximize the properties of the two different compositions.

Methods

X-ray diffraction experiments were carried out using the modified conventional Philip vertical goniometer utilizing CuK$_\alpha$ radiation. A diffracted beam analyzing crystal was used for energy discrimination. The diffractometer was modified so that the experiment can be carried out in transmission as shown in Fig. 1. The fiber axis can be rotated with respect to the scattering plane. At 0° φ angle, the fiber axis is perpendicular to the scattering plane; hence, by tilting the fiber on the angular range θ–2θ, an equatorial scan is achieved. With φ=90° degree angle, a meridonal scan is accomplished by tilting the fiber over the angular range θ–2θ. Steps of 5° interval for the fiber direction rotation are used. In this way, the Bragg condition of coupling θ and 2θ is satisfied at all angles. By staying at the peak 2θ location, the sample can be rotated about φ to determine the angular spread, thus determine the Herman's orientation function. These fiber materials are not conventionally crystalline; hence the term 'degree of crystallinity' will be used to indicate the measure of chain ordering as indicated by the presence of distinct peaks in the diffraction results. This 'degree of crystallinity' is estimated from a plot derived by the summation of the 19 scans from 0 to 90 in φ to cover the full quadrant of the fiber diagram. The ratio of the ordered peak area to the total peak area is then defined as this 'degree of crystallinity'.

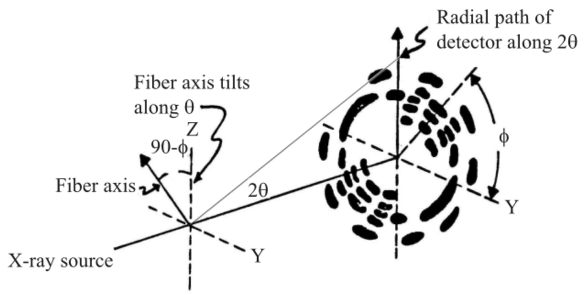

Fig. 1 Schematic diagram of experimental setup for WAXS experiment

The small angle X-ray scattering experiment is carried out using both the in-house system and the one that is set up at X-11 beamline at NSLS (National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY) pin-hole system. Because of the low scattering intensity, a direct detection CCD camera from Princeton Instrument is used. The accumulation was carried out by summation over several frames of data acquisitions.

Thermal analysis experiments were carried out on the as-spun and heat-treated fibers. A PerkinElmer DMA7 configured in the TMA mode was used to determine fiber length change with temperature on single filaments about 25 μm in diameter. Static tensile loads ranging from 10 to 100 mN were employed in these experiments. Thermally stimulated current (TSC) experiments were performed on a Solomat TSC/RMA 91000. The TSC experiments were conducted in the depolarization mode. For TSC experiments, thin films were prepared in the commercial plant, using process conditions similar to those used to melt spin fibers. These films had nominal thicknesses of 25 μm. Heat treated films were prepared using the commercial protocols. Films were placed between two electrodes with the plane of the film perpendicular to the direction of the applied static electric field. The field was provided by a static voltage of 100 V at 120°C for 2 min. After this polarization operation the film was rapidly quenched to –150°C. Depolarization current was monitored as the film specimen was heated from –150 to 160°C at 7°C min^{-1}.

Results and discussion

Single filaments of LCP compositions chosen for this study have been tested for tenacity and modulus. The room temperature modulus and tenacity values for the as-spun and heat treated Vectran® and COTBP fibers are shown in Table 1. On heat-treatment, an increase in tenacity can be observed in both fibers, however there is a larger increase in modulus for COTBP. As previously indicated, the commercial heat treatment protocols are different for the two compositions.

Thermal analysis

In previously reported DMA experiments, the α-relaxation for Vectran® was identified with a relaxation process observed at ~100°C, an additional dispersion peak observed between 50 and 65°C. While the relaxation at 100°C is often described as the 'glass transition', a typical glass transition involves large scale segmental motion that is not expected to occur in these highly oriented LCP fibers in as much as they retain their orientation to temperatures well above 100°C [8, 9]. The origin of this process is not clear; however, it is speculated to be the result of slipping of oriented entanglements in the LCP fiber [9]. TMA results for single filament, as-spun Vectran® with increasing static tensile load on the filament are shown in Fig. 2. For this oriented filament, the contraction in fiber specimen length with increasing temperature is the consequence of the conformational rotations occurring along the extended polymer chain which decreases the end-to-end distance. There are mechanical elements which transmit this decrease along the length of the filament. In the vicinity of 50 to 60°C, there is what appears a partial failure of the ability of these elements to transmit the tensile stress along the filament. At low static loads the fiber will continue to contract after this partial failure. At higher static loads, the fiber extends to failure after the partial failure event. Even when the filament does not expand to failure, that failure is not catastrophic. Rather, it occurs over a wide temperature, suggesting that there remain intermolecular mechanical elements that are resisting the failure process.

Table 1 Physical properties of Vectran and COTBP

	As-spun	Heat treated
Vectran tenacity/ g d^{-1}	11	27
Vectran modulus/ g d^{-1}	525	550
COTBP tenacity/ g d^{-1}	8.5	21
COTBP modulus/ g d^{-1}	520	880

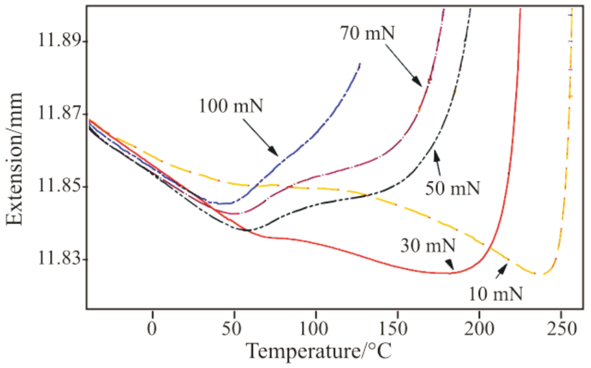

Fig. 2 TMA of as-spun Vectran® fiber with increasing tensile loads

When considered in detail, the TMA results provide some indications of the nature of the mechanical elements that transmit the stress. First of all, these elements appear to be discreet in nature. That is to say, the thermally induced motions of the oriented macromolecules that make up the internal solid structure result in the partial failure of the filament specimen reproducibly in the same temperature range regardless of the applied tensile load. Secondly, even after this partial failure, the mechanical elements are present in a manner that resists catastrophic failure over a wide temperature range. This suggests that these mechanical elements are weakened by the thermally induced motion of the oriented macromolecule, but not eliminated. Models for the molecular structure of these wholly aromatic polyesters have indicated that while the polymer chain may extended in an oriented conformation, it is unlikely that these types of macromolecules are strictly rigid [10]. Considering the possible modes of aggregation for a polymer that is oriented but not strictly rigid, it is necessary to allow that oriented entanglements can exist between oriented polymer molecules. These oriented entanglements would represent discrete mechanical elements capable of transmitting mechanical stress along the filament. In addition, the mechanical integrity of these oriented entanglements would be sensitive to the stress applied to the filament as well as the local thermally induced motion at the site of the

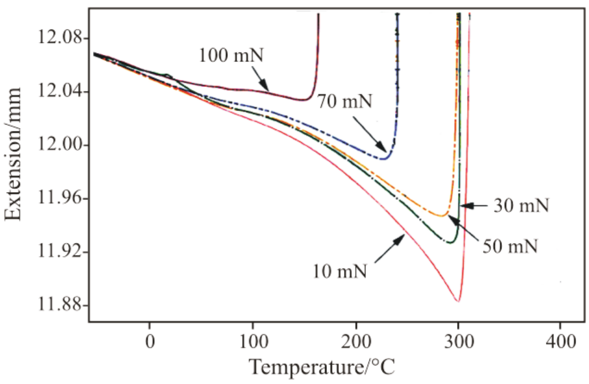

Fig. 3 TMA traces of heat treated Vectran® monofilament with increasing tensile loads

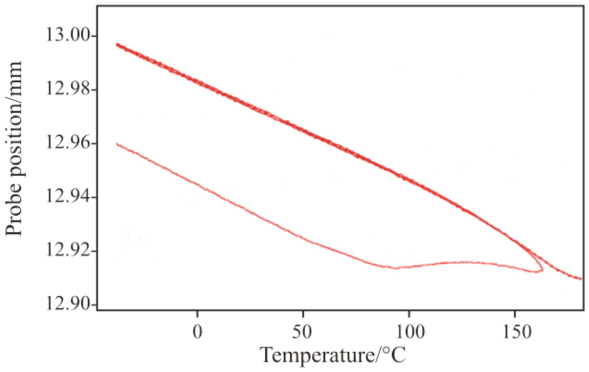

Fig. 4 Heat-cool-heat TMA of as-extruded Vectran® film

entanglement. This behavior appears to be reflected in the TMA results shown in Fig. 2.

Figure 3 shows TMA results for heat treated single filaments of Vectran®. For this case the partial failure process between 50 and 60°C is barely visible. If it is assumed that the oriented entanglements are the operative mechanical elements, then the heat treating process has resulted in them being redistributed in a manner that increases the resistance to thermally induced failure. Similar to the as-spun filaments, failure can be induced at a lower temperature with the application of higher tensile load; however, unlike the as-spun filaments that start to show failure at about 50°C, the lowest temperature failure for heat treated filaments with the highest load, 100 mN, is slightly above 150°C.

Figure 4 shows TMA results for an as-extruded oriented Vectran® film using a heat-cool-heat program. The partial failure behavior observed for as-spun fiber is clearly observable on the first heating of the film, but is not seen on the subsequent cooling or reheating segments.

This partial failure process is taken to be representative of the behavior of the mechanical elements in the fiber that is transmitting the force of thermally induced shrinkage through the filament. This process is also taken to represent the additional dispersion peak in the vicinity of 65°C that is reported in DMA results. Assuming these mechanical elements are oriented entanglements, the transmission of stress through the filament occurs by the mechanical integrity of these entanglements. The disposition of these entanglements appears to be altered during the first heating segment treatment. The film shows a non-recoverable elongation on the first heat, but on subsequent cooling and reheating, the mechanical integrity of the film is retained over the entire temperature range. If the mechanical elements are taken to be these oriented entanglements, then the slipping can occur until one entanglement engages another entanglement. At that point slipping is arrested and any further slip would occur with difficulty. On the first heat, slipping occurs at the temperature of partial failure. Cooling before complete failure results in entanglements interacting with each other in a manner that prevents slipping. On reheating, those interacting entanglements remain intact, and the force of contraction is transmitted along the filament over the entire temperature range.

In previously reported measurements, the glass transition at 100°C observed in DMA of Vectran® is only weakly detected. Temperature dependent WAXS, not reported here, indicate that fiber orientation is retained to high temperatures. Clearly the α-relaxation process of a persistently oriented polymer does not represent the same type of long range segmental motion that is observed in typical polymers. Motion of that type would result in loss of orientation. Thermally stimulated current (TSC) is a non-calorimetric technique that probes the current produced when molecular scale dipoles undergo motion during relaxation processes. Figure 5 shows the depolarization current profile for an oriented as-spun Vectran® film. A large relaxation peak is observed just above 100°C.

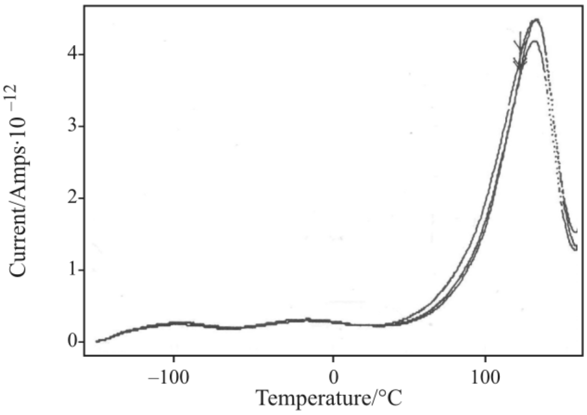

Fig. 5 TSC depolarization current of as-extruded Vectran® film

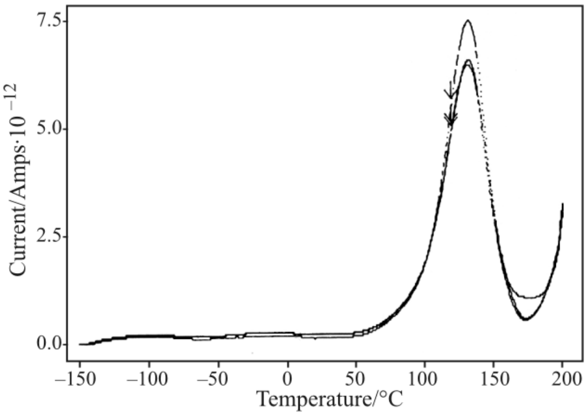

Fig. 6 TSC depolarization current of heat treated Vectran® film

Figure 6 shows the TSC depolarization current profile for an oriented heat treated Vectran® film. The qualitative features of the heat treated film are nearly exactly similar to that of the as-extruded film.

It has been suggested that the inability of the Vectran® chains to undergo large scale segmental motion is a consequence of the chains being physically constrained in a manner that maintains relative chain orientation over a wide temperature range [11]. This constraint restricts the large scale segmental motion, but does not interfere with rotational relaxation of polar structures along the main chain of the macromolecule. The depolarization current observed in both as-extruded and heat treated film is taken as an indication of these rotational motions occurring at the temperature reported from DMA results. The constraints to loss of orientation at with increasing temperature could be provided by the occurrence of oriented entanglements. Based of the similarity of the TSC results for both as-extruded and heat treated film, heat treatment does not appear to diminish the rotation of these polar structures, suggesting that heat treatment does not result in a drastic change in the mode of solid state aggregation in the fiber.

Wide angle X-ray diffraction (WAXS)

The nature of the solid state order of Vectran® has been the topic of many investigations. It has been described as 'paracrystalline' [12, 13] to indicate a quasi-three-dimensional order, but it has not been possible to describe a unit cell. There is clearly molecular scale ordering, but this ordering is unlike the conventional crystal building. The notion of 'degree of crystallinity' in Vectran® LCP is still a very difficult and unresolved issue. There are discrepancies between the WAXS (wide angle X-ray scattering) and DSC (differential scanning calorimeter) measurements. Butzbach *et al.* [14] reported for HBA/HNA 58/42 sample, the degree of crystallinity is more than 60%. The crystals are far from being perfect since the enthalpy and entropy of the transition are 10–20 times smaller than expected. Blundell [15], however, suggested that the degree of crystallinity should be lower and explained that discrepancies exist between WAXS and DSC because of melting out small micro-crystals that are too small to give sharp X-ray diffraction peaks.

The as-spun fibers are oriented but not fully organized in three dimensions. The sequence of structural units along the oriented chain is aperiodic, and it may be due to this aperiodic nature of the polymer chains that molecularly well organized or conventional crystallized structures cannot develop. Figure 7 shows the resulting 3-D fiber diffraction patterns for the as-spun and heat-treated Vectran® and COTBP. Each diagram consists of 19 spectra. The spectrum in front corresponds to the data acquired at $\phi=0$ is the equatorial scan and when $\phi=90$ is the meridional scan. The diagram for the as-spun Vectran® and COTBP fibers are very similar. They both consist of a strong equatorial peak and probably a smaller shoulder peak on the right.

Differences were detected between the structural responses in the as-spun fibers as well as the heat-treated fibers as a function of temperature. A full extracted parameter describing the molecular structure is given in Table 2. The *d*-spacings are extracted from peak positions, the 'crystallite' size is estimated from the peak width and the orientation is determined by counting while rotating the fiber perpendicular to the scattering plane. The peaks close to the equator can be roughly indexed to an orthorhombic structure while the higher angle meridional peaks are due to the aperiodic structure. Hence, they

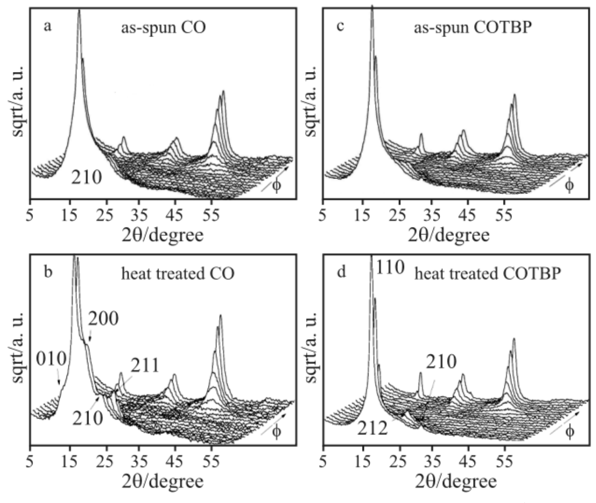

Fig. 7 WAXS of as-spun and heat-treated CO Vectran® and COTBP at ambient temperature

Table 2 XRD extracted parameters for as-spun and heat-treated CO and COTBP

CO as-spun crystallinity=39%							CO heat treated crystallinity=48%						
Peak	‘*d*’/Å	*hkl*			Size/Å	*f*	Peak	‘*d*’/Å	*hkl*			Size/Å	*f*
							E	5.28	0	1	0		
E	4.55	1	1	0	31	0.942	E	4.63	1	1	0	39	0.941
							off E	4.51	1	1	1		
							E	4.04	2	0	0		
off E	3.35	2	1	1			off E	3.22	2	1	1		
E	3.23	2	1	0			E	3.26	2	1	0		
M	6.9		1st		51	0.933	M	6.94		1st		63	0.937
							H	3.42		2nd			
M	3.08		3rd		27	0.931	H	3.07		3rd		32	0.935
M	2.08		4th		48	0.905	M	2.09		4th		44	0.91
COTBP as-spun crystallinity=47%							COTBP heat treated crystallinity=59%						
Peak	‘*d*’/Å	*hkl*			Size/Å	*f*	Peak	‘*d*’/Å	*hkl*			Size/Å	*f*
E	4.49	1	1	0	60	0.96	E	4.49	1	1	0	74	0.974
off E	3.27	2	1	1			off E	3.29	2	1	1		
E	2.57	1	2	0			E	2.56	1	2	0		
M	6.07		1st		85	0.961	M	6.13		1st		92	0.971
H	3.24		2nd		49	0.939	M	3.26		2nd		65	0.949
							M	3.01		3rd			
M	2.09		4th		52	0.91	H	2.1		4th		61	0.934

E=equator, M=meridian

represent a quasi-order structure due to the random monomer sequencing along the chain and can be crudely indexed as (001) type reflections. The lattice parameters for the orthorhombic structure are roughly a=7.96 Å, b=5.69 Å and c=12.54 Å. Because of lack sufficient peaks, this structure is also referred to as pseudo-hexagonal.

As indicated in Fig. 7, the development of 3 additional peaks in Vectran® and not COTBP can be observed in the heat-treated samples, indicating a much improved molecular organization in Vectran®. The molecular organization of the as-spun Vectran® is poor, being hindered by the random sequencing of the HNA and HBA monomer units along the chain. On heat treatment, while molecular mass increases have been reported, there are definite changes taking place in the molecular organization of the Vectran® chains. The appearance of three new reflections suggests that Vectran® chains are attempting to form a three-dimensional crystal structure.

There are also shifts in the *d*-spacing in Vectran® fiber that are not observed in COTBP, as listed in Table 2, suggesting a separation of the most electron dense region 110 planes. In addition, the 'degree of crystallinity' increases from 39 to 48% for Vectran® and 47 to 59% for COTBP upon heat treatment. There is only a small increase in the apparent 'crystallite' size, measured from the (110) reflection. This increase is significantly more in COTBP than in Vectran®. There is a slight improvement in orientation function for both COTBP and Vectran®. There is no significant change in the meridional scattering between the as-spun and heat-treated fiber, indicating that there are no changes in the monomer sequencing.

Small angle X-ray diffraction (SAXS)

SAXS measurements were also carried out on the as-spun and heat treated Vectran® fibers at ambient temperature. The results are shown in Fig. 8. The as-spun fiber exhibits a horizontal streak through the origin which is normally attributed to needle shaped voids existing in the fiber with their long axes aligned parallel to the fiber direction. The SAXS patterns for the heat treated fiber are surprising because these patterns have not previously been observed. They are only observable as a consequence of the high angular resolution possible in the apparatus used in the experiment. In addition to the lateral streak mentioned above, for Vectran® there is the appearance of an 'X' pattern. The angle of the 'x' with respect to the fiber axis is about 10°. This likely reflects the diffraction pattern from helical structures or sinuosity of the packing order in Vectran® [16]. For COTBP, the changes on heat treatment are more subtle. There is a slight increase in SAXS intensity along the axis of the fiber. Real-time SAXS during heat treatment show more distinct changes in the SAXS pattern [17].

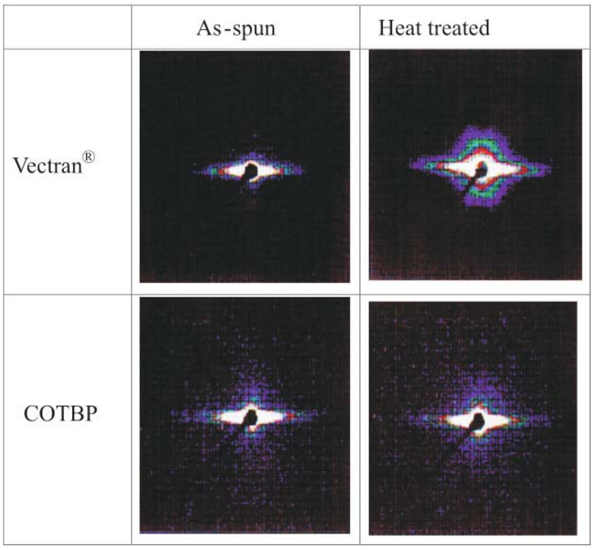

Fig. 8 SAXS of as-spun and heat-treated Vectran® and COTBP at ambient temperature

The SAXS patterns for Vectran® and COTBP fiber suggest that a reorganization of the solid state occurs on the molecular scale that is difficult to associate with conventional crystallization and does not involve the rearrangement of structural units along the length of the LCP chain. SAXS patterns similar to those observed in Fig. 8 have been well documented in the annealing of oriented polypropylene. Historically, this behavior has been attributed to the clustering of entanglements that were considered defects to the orientation of the polypropylene chains. The mobility of these defects was made possible as a result of the thermally induced local changes in segmental conformation [18].

Similarly, it is postulated that the SAXS patterns observed for Vectran® and COTBP are due to the clustering of oriented entanglements at the molecular level during heat treatment of fiber. Isolated entanglements will not generate sufficient density contrast for SAXS to be observed. These entanglements have to be clustered and organized locally over 100–400 Å or larger in order exhibit the pattern as observed in SAXS. The entanglements can cluster forming regions of local coherence and the migration of entanglements leaves local regions where the chain sections are highly parallel.

Conclusions

The concept of oriented entanglements has been invoked as the important, discrete mechanical elements that transfer stress along the length of a wholly aromatic polyester LCP filament under tensile load. These entanglements are the mechanical elements that mediate the tensile properties of the filaments. Before heat treatment, spatially distributed entanglements do not provide enough mechanical integrity to prevent slipping of oriented chains relative to each under tensile load. Thermally induced slipping can be observed in the TMA of as-spun fibers. Heat treatment results in the clustering of these oriented entanglements, and, by contrast, after heat treatment, clustered entanglements provide a higher level of mechanical integrity and suppress chain slippage under tensile load, which can be observed as a loss of thermally induced slipping for heat treated fibers.

Using this mode of interpretation, the change in the internal structure of the filament during heat treatment is subtle. The thermal energy provides the driving force for the change in the disposition of the oriented entanglements from spatially distributed to clustered. The clustered entanglements enhance the ability of the filament to transmit stress along its length, which relates to the increase in tensile properties on heat treatment. Clusters form regions of high density and result in density fluctuations along the filament length that can be observed as SAXS patterns with spacings on the order of 100–400 Å. These clusters also provide an avenue to give physical meaning to the mechanical elements in aggregate theory. The close proximity of chains in these clustered regions may produce the pseudo-crystallinity that is observed in the WAXS patterns. Since there is little immobilization of the chain segments as a consequence of entanglement clustering, the rotational relaxation along the LCP chain is unaffected by heat treatment as observed in TSC results. Future publications will examine the details of the dynamics of the entanglement clustering process and the mechanism of tensile property enhancement as a consequence of entanglement clustering [17].

Acknowledgements

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