

Influence of Molecular Orientation on the Melting Behavior of Poly(phenylene sulfide) Fibers

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ABSTRACT

The influence of molecular orientation on the melting behavior of draw-annealed poly(phenylene sulfide) fibers is investigated in the present paper. Tools used to probe the investigation were differential scanning calorimetry, polarized light optical microscopy, wide angle X-ray diffraction, and small angle X-ray diffraction. It is shown that molecular orientation in the crystalline and amorphous regions play a key role in crystal rearrangement during melting. A probable mechanism by which amorphous orientation influences crystal rearrangement is also discussed.

INTRODUCTION

Poly(phenylene sulfide) is an important engineering thermoplastic for applications that require high temperature resistance and good chemical resistance. Since discovery, it has been used in products manufactured by injection molding processes. Therefore, the majority of the literature available deals with crystallization kinetics of PPS [1-7]. Its good resistance to high temperature and chemicals make it very suitable in the form of fiber to be used in filtration applications such as the paper industry and power plants.

Investigation of the process-structure-properties relationship for a variety of thermoplastic polymers in the fiber form, such as polyethylene terephthalate (PET), nylon, polyolefins, have been reported in several research papers. It is reported that molecular orientation increases the rate of crystallization of fibers [8-11]. Influence of orientation on melting behavior in isotactic polypropylene fibers was studied by Samuels [12]. Prevorsek et al. [13] investigated thermal response of PET fibers in terms of crystallites rearrangement.

Detailed investigation of process-structure-property relationship in melt spun PPS fibers was conducted by us, and findings are reported in our recent publications [14-16].

The present study focuses on the role of molecular orientation on the melting behavior of PPS melt spun fibers. These morphological aspects have a significant influence on the properties of the fibers, and it is important to understand the key factors that affect the melting behavior in a unique way.

MATERIALS AND METHODS

Materials

Proprietary Fortron® PPS resin in the pellet form was provided by Ticona Polymers. The melt flow rate of this resin was measured in accordance with ASTM standard [17], and was found to be around 61 g/10 min at 315°C.

Methods

The pellets were extruded using a Fourné single screw extruder, and spun into multifilament fibers using a 12 holes spinneret. Each capillary was 800 µm in diameter with an l/d ratio of 10. Extrusion temperature, throughput, and take-up speed were 315°C, 1 g/min/hole, and 1750 mpm, respectively. The as-spun fiber (AS) was drawn using a SAHM drawing unit. Fibers were drawn at temperatures (DT) of 90°C, 95°C, 100°C, and 115°C. Each of the drawn fibers were annealed (DA) at 150°C in a continuous operation at a speed of 15±2 mpm. DA fibers are labeled as DA1, DA2, DA3, and DA4 in the order of increasing DT.

A Mettler Toledo DSC 822e was used to study the melting and crystallization behavior of the pellets, drawn annealed fibers, and a semicrystalline film produced from these pellets. Crystalline film (CF) was produced by hot pressing the pellets at 315°C, and then slowly cooling them to develop the crystalline morphology. Samples were heated to 325°C at a rate of 20°C/min in a nitrogen atmosphere. The draw-annealed fiber (DA2) was heated (DA2HT) in DSC to 280°C at the rate of 10°C/min and then cooled rapidly at a rate of -

100°C/min. It has been reported in the literature by various investigators, a good account of which is provided by Jaffe et al. [18], that the mode of packing the fibers in DSC pan influences its thermal response. Especially when packed by chopping, the fibers undergo relaxation during the heating cycle of DSC, and no longer represent the original sample. Therefore, preventing such relaxation during heating is important to understand the thermal and stress history of the original sample. Accordingly, in the present research fiber samples were carefully knotted before placing them inside DSC pans for studying their melting behavior.

Birefringence (Δn) was determined by polarized light optical microscopy using a 20 order Ehringhaus compensator. Crystalline orientation (f_c), crystallinity (X), and crystal size (L_{hkl}), were calculated from wide-angle X-ray diffraction (WAXD) patterns obtained using the Molecular Metrology WAXD system. Amorphous orientation (f_a) was calculated from birefringence and crystalline orientation (f_c). Long period was determined from small angle X-ray diffraction (SAXD) patterns. Details of above morphological evaluations are provided elsewhere [14].

Surface morphology of select fiber was studied using LEO SEM. The draw-annealed fiber was carefully cut longitudinally using a razor blade to reveal internal structure. Since samples were not gold coated, a lower beam voltage of 1 kV was used to prevent sample charging.

RESULTS AND DISCUSSION

Figure 1 shows the comparison of melting behavior of draw annealed fibers with that of the as-spun fiber, pellets, and crystalline film.

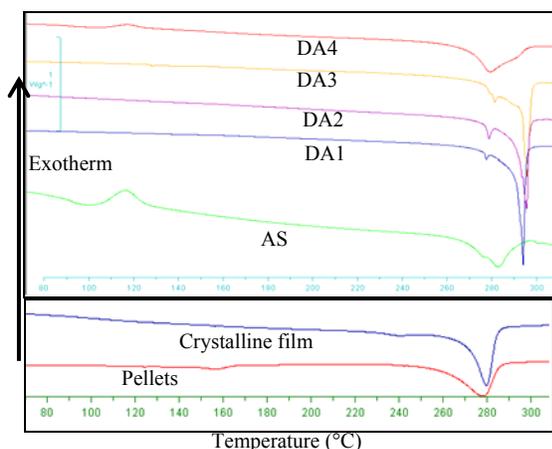


FIGURE 1. Effect of drawing temperature on the thermal behavior of drawn fibers.

In the case of as-spun fibers, spun under the conditions mentioned in experimental section, peak melting temperature is observed around 280°C. It is similar to that observed in the as-received pellets. Upon drawing up to DT of 100°C, draw-annealed fibers exhibit a very small endotherm at 280°C and the major endotherm with considerably higher peak melting temperatures of around 295°C. Also the melting endotherms are much sharper. While performing the thermal evaluations using DSC, the fiber samples were carefully knotted to prevent the stress relaxation at higher temperatures inside the DSC pan. Upon drawing beyond DT of 100°C, the melting endotherm of draw-annealed fibers becomes broader with a peak at around 280 °C.

A study was conducted to investigate if the draw-annealed fibers possess a different crystal structure that exhibits higher T_m or if the crystal structure reorganizes during heating in DSC. For this purpose, one of these draw-annealed fibers drawn at 95°C was heated in DSC to 280°C at the rate of 10°C/min, and then cooled rapidly at the rate of 100°C/min. The temperature of 280°C was chosen, since at this temperature, the draw annealed fibers are still not melted. The WAXD pin-hole pattern of this heat treated fiber was compared with that of the draw-annealed fiber.

The pin-hole patterns are shown in Figure 2. For the purposes of comparison, WAXD evaluation of crystalline film was also carried out. Corresponding quantitative data of crystallinity and crystal size are given in Table I.

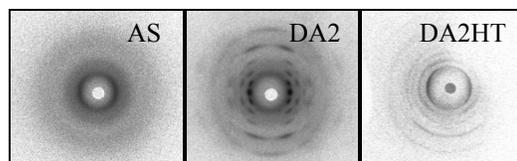


FIGURE 2. WAXD pin-hole patterns of fibers (fiber axis vertical).

The level of crystallinity in the crystalline film, as-spun fiber, DA2 fiber and DA2-HT fiber is around 37%, 10%, 33% and 46%, respectively. The peak melting temperature of the crystalline film (Figure 1) is similar to that of low crystallinity and poorly oriented as-spun fiber. The latter clearly exhibits a cold crystallization peak on heating in the DSC around 115°C, so much of the crystallization occurred at this temperature. The WAXD pin-hole pattern of DA2 fiber (Figure 2) shows highly oriented crystalline structure. However, upon heat treatment, the patterns show some loss in orientation with wider arcs. The crystal width calculated from

the intensity distributions of planes (110) and (200) in DA2-HT fiber is 316 Å and 107 Å, whereas that in DA2 fiber is 69 Å and 50 Å, respectively, and a significant increase in crystal width is observed upon heat treatment at 280 °C. Thus it can be deduced that the crystals melting at higher temperatures of 295 °C are primarily formed by rearrangement during heating in the DSC. The degree of crystallinity in DA2-HT fiber is around 46%, as compared to that of 33% in DA2 fiber. Hence, it can be stated that the crystal growth may have taken place to some extent by incorporating molecular chains lying in some of the highly ordered non-crystalline regions adjacent to the existing crystal, and also by combining neighboring crystals.

Absence of high temperature melting peak in poorly oriented amorphous as-spun fiber, and in unoriented crystalline film suggests that during heating, such rearrangement may not have taken place in the absence of molecular orientation. This clearly indicates that molecular orientation is playing a role in crystal rearrangement, that subsequently leads to larger crystals in draw annealed fibers, which melt at higher temperatures.

TABLE I. Morphological properties of the samples.

Sample	X	Δn	f_c	f_{am}	L (Å)	L_{hkl} (Å)	
						$L_{(110)}$	$L_{(200)}$
Pellets	35					65	60
AS	10	0.13			ND	28	
DA1	33	0.27	0.76	0.85	13 2	90	66
DA2	33	0.27	0.93	0.77	83	69	51
DA4	28	0.16	0.68	0.39	12 2	92	81
DA2HT	46					316	107
CF	37					109	116

Where, X is the degree of crystallinity, Δn is the birefringence, f_c is the crystalline orientation function, f_{am} is the amorphous orientation function, L is the long period, and L_{hkl} is the crystal size.

It is not that only the larger crystal size is the cause of high melting peak in DSC endotherm. The crystal width in the crystalline film is around 110 Å based on (110) and (200) planes, as compared to 69 Å and 50 Å, respectively in DA2 fiber. In spite of consisting of larger crystals, peak T_m in crystalline film is at around 280°C whereas that in DA2 fibers is around 295°C. Thus it can be stated that highly ordered inter-crystalline region is providing hindrance to melting of the crystals when the sample is constrained during

heating and hence requires higher temperatures for crystal melting. Thus the role of molecular orientation in melting behavior of highly oriented PPS fibers may be two fold: to act as a catalyst for further crystal rearrangement and also to provide resistance to melting of crystals through the presence of highly ordered non-crystalline region. Yamada et al.[19] reported an increase in melting temperature of highly oriented isotactic polypropylene films and attributed this to an increase in amorphous orientation. Through extensive study on melting behavior of isotactic polypropylene fibers, Samuels [12] concluded that the multiple melting endotherms in oriented and restrained fibers are the manifestations of orientation in amorphous regions above a certain minimum value of f_{am} . The increase in melting temperature was attributed to decrease in the configurational entropy of molecular chains in oriented amorphous regions. Observed increase in melting temperature of draw-annealed PPS fibers in the present research can similarly be attributed to high level of amorphous orientation. One of the probable mechanisms by which highly oriented amorphous domains contribute to increase in T_m is discussed below.

Through WAXD studies, it is seen that crystal size increases more than two fold after heat treating the fibers, whereas crystallinity increases by only around 13%. While heat treating PPS samples in DSC in the present research, although the sample was knotted to provide restraint, some loss of crystalline orientation suggests that contraction may have taken place to a certain degree and further rearrangement of crystallites may have happened. Presence of fibrillar morphology in the draw annealed PPS fibers is evident from the SEM micrographs as shown in Figure 3.

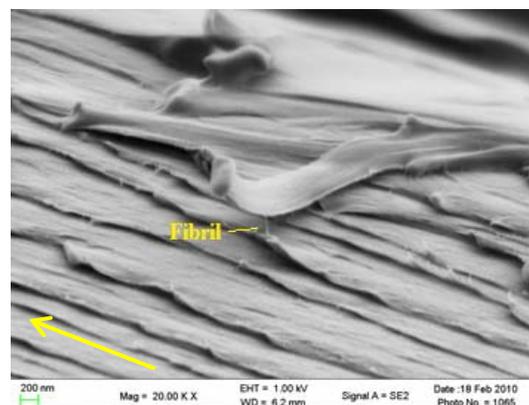


FIGURE 3. SEM micrograph of two zone draw-annealed fiber. (Arrow indicates fiber axis).

In a study on thermal contraction of drawn PET fibers, Prevorsek et al. [13] reported that up to 10% contraction, only the amorphous domain between crystallites shrink, whereas there is no relative displacement of neighboring microfibrils. However, at higher level of contraction, 20% and more, based on WAXD, SAXD, and infrared spectra, they reported that neighboring microfibrils displace with respect to each other. Carr and Ward [20] have shown that entanglement density is high in the case of PPS as compared to PET. Hence it may be possible that relative displacement of neighboring microfibrils happen at lower contraction level in the case of PPS. If the neighboring microfibrils move relative to each other, one of the possibilities may be that crystallites in one microfibril move and sit next to the neighboring microfibril, rather than remaining in skewed arrangement. The 10% increase in crystallinity may suggest that some of the interfibrillar region may have been converted to crystalline region. Therefore, without increasing the crystallinity to a large extent, crystal dimension perpendicular to fiber axis (crystal width) increases more than two fold. It is important to note that, in order for this phenomenon to occur, chains in interfibrillar domain need to be oriented so that some mobility and minor rearrangement in structure makes them go into crystallites. It may also be possible that some of the crystallites break and join the newly formed crystallites out of interfibrillar domains. Thus the larger crystals formed due to one or more of the above mechanisms will melt at higher melting temperatures. This very well explains the observed increase in T_m of PPS fibers in the present investigation, and the role of amorphous orientation for this phenomenon to occur.

CONCLUSIONS

Based on extensive morphological evaluations of draw annealed PPS fibers upon thermal exposure, it is shown that the melting behavior of fibers is greatly influenced by the molecular orientation, both in the crystalline and amorphous regions. Further, a mechanism by which amorphous orientation influences the melting behavior is proposed. A highly oriented intercrystalline region is essential for the crystal rearrangement that takes place upon thermal exposure. Such a rearrangement leads to a considerable increase in crystal width with a slight increase in crystallinity.

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