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A New Technique for Generating Regularly Spaced Crazes to Facilitate Piece Dyeing of Polypropylene Filaments

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ABSTRACT: The aim of this study was to investigate crazing that generates regular crazes in polymeric fibers. For carrying out this study, we designed and fabricated an experimental apparatus for generating crazes on polypropylene (PP) filaments. By an optical micrograph and a laser scanning micrograph of the surface and cross-section of the filaments, it was confirmed that the crazes were generated on the surface of the filaments. Optical microscopes and measurements of the craze morphology on the filaments showed that approximately 30–50% of the contact area was crazed. As the crazing tension increased, the interval between the crazes increased, but the width of the crazes did not change significantly. Moreover, it was confirmed that the filaments had a homogenous crazed structure and pores were formed in their structure. The crazing process did not affect the strength of the crazed filaments significantly; the crazing process decreased the light transmittance of the filaments. The acid dyeing was adsorbed onto crazed region of PP filaments. These crazes in the filaments have the potential to lead to new methods for dyeing PP fibers. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 3564–3569, 2013

KEYWORDS: crazing; processing; fibers; dyes/pigments; poly(propylene)

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INTRODUCTION

A piece dyeing of polypropylene (PP) fibers is difficult by conventional industrial processes, except by specific techniques such as polymer blending,[1] chemical modification,[2] surface modification,[3,4] and supercritical dyeing.[5] This fact is undesirable and disadvantage for textile fabrics of PP.

Crazing is an important fracture mechanism in polymers. Crazes often represent the first stage of the fracture process in polymers in relation to molecular entanglement and the characteristic ratio of the intrinsic flexibility and rigidity of a molecular chain.[6–9] While the structure of crazes is similar to that of a sponge containing fibrils and voids having dimensions of the order of nanometers, it is quite different from that of cracks.[10] Crazes show elastic characteristics while maintaining the tensile strength of the material. If the crazing process in polymers can be controlled, the process can be used to prepare mesoporous films and fibers in a simple manner. By generating crazes in a polymer and by its composite structure as to a crazed region with a noncrazed region regularly, it is possible to obtain an anisotropic transparent polymer; such a polymer appears as a transparent film when viewed from the front and as an opaque film when viewed from the side.[11–14] The formation of crazing regions in PP filament fibers is investigated. The crazes are generated by a homogeneous and controllable process in such a manner that they are evenly distributed along the filaments.[13] This process can help in fabricating a nanostructured material that can be used for many purposes or functions.[11] Continuous and controlled crazes result in structures with favorable properties.[11] In this research, we attempt to modify PP multifilaments by using the crazing process. We aim to realize continuous and controlled crazes on the PP multifilaments and evaluate the structural parameters of the crazed filaments. And we especially focus on the pores (voids) in the crazed areas for considering the feasibility of piece dyeing.

MATERIALS AND EXPERIMENTAL METHODS

PP multifilaments that were not stretched and that were spun at the Industrial Technology Center, Gifu Prefecture Government, Japan, were used as raw and unprocessed samples in this study. The properties of the multifilaments are listed in Table I.

An experimental apparatus was designed for crazing the filaments and generate regular crazes and necking (Figure 1). In this apparatus, the filaments were pulled under a certain tension through a path having a defined bend. A bending section was

Table I. Multifilament for Crazing Process

Sample	PP multifilament
Diameter (μm)	Approx. 45
Diameter [*D*]	Approx. 440
Filaments	36
Drawing ratio	Unstretched
MFR (g/10 min)	Approx. 60
Yield stress (MPa)	17
Young's modulus (MPa)	165
Breaking stress (MPa)	234
Breaking strain (%)	1900
Crystallinity (%)	29 ΔH_m^0 (= 870 kJ/mol)

included for bending the filaments by a specific amount under a controllable axial tension. The axial tension could be measured and controlled for creating certain crazing conditions for generating regular crazes and necking in the filaments. The bending section had a roller bottom for taking the filaments out. A blade was positioned on top of the bending arm. The bending-arm angle was adjustable in the horizontal plane. The bending section included a bending arm that had a sharp blade fixed on top. This apparatus was mounted on the bottom jaw of a tensile testing machine (Orientech Tensilon/UTM-4-200, Tokyo, Japan) fabricated by Toyo Baldwin. One end of an unprocessed filament specimen was fixed to the upper jaw of the machine, and a defined weight was hung from the other end of the specimen, which had a length of about 30 cm. When the bottom jaw moved down, it drew the crazing unit down, and as a result, the filament was crazed. The crazing process was performed at various stresses in the range 0–12 MPa. The elevation and the bending angles of the bending arm were 30° and 155°, respectively. The process speed was 40 mm/min and the experimental tests were performed at room temperature.

Observation of the Crazed Filaments

An optical microscope using transmitted light and manufactured by Nikon (MM-22, Tokyo, Japan) was used to observe and photograph the surface and cross-section of the crazed filaments. The widths of the periodic crazed structure and the interval between the crazes were measured from the photographs of the crazed filaments. Moreover, to observe the cross-section of the filaments, an epoxy resin was put around the samples from the crazed multifilaments and the resin was then hardened at 65°C. These filaments were cut vertically along their axis, and their cross-sections were then observed with the optical microscope. Furthermore, to observe the porosity of the surface of the crazed filaments, the transmitted light and reflected light in the optical microscope were cut off. White light was then shed on the filaments and their surfaces were observed. The morphology of the filament surface was evaluated by using a scanning electron microscope (SEM: Hitachi PC-SEM S4300, Tokyo, Japan). The sample was coated with a thin layer of Pt/Pd to facilitate observations. A laser scanning microscope (LSM), LSM 5 PASCAL model manufactured by ZEISS (Oberkochen, Germany), was used to observe the surface and internal structure of the filaments. In the LSM, the sample is irradiated with a laser and the reflected light from a particular collection point is then recorded after passing through a pinhole placed at the imaging point of the objective lens' light path. While the object is scanned, the images of the surface of the sample and its internal structure are formed.

RESULTS AND DISCUSSION

Structure of the Crazed Filaments

Various types of polymers may be subjected to crazing. In addition to occurring in glassy thermoplastics, where they are clearly seen because of the transparency of the material, crazes or at least craze-like structures occur in semicrystalline thermoplastics too, such as polyethylene and PP.[15] Generally, the crazes are initiated preferentially at surface imperfections such as scratches and adventitious particles of various kinds. Generally, there is an induction period for applied stress. The number of crazes per unit volume is saturated, presumably because all heterogeneous nuclei are exhausted.[15] The crazes that are generated because of bulk surface imperfections are usually heterogeneous and have an irregular distribution along the filament length. Weichold et al. reported that during solvent crazing, the number and distribution of the crazes along the filament are random.[16] Figures 2 and 3 show the typical photographs of the

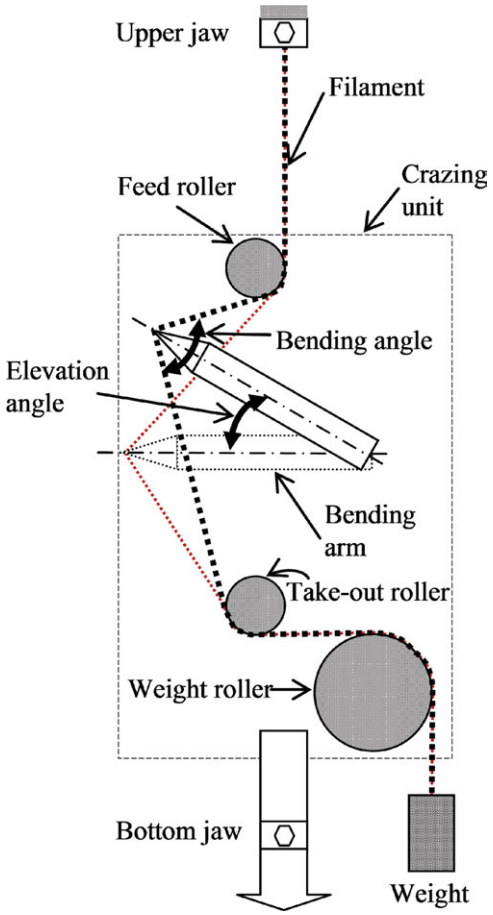

Figure 1. Experimental apparatus designed for crazing the filaments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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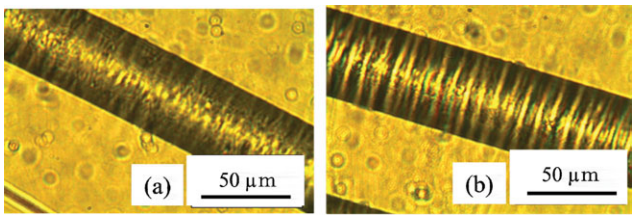

Figure 2. Optical micrographs of the PP filament: (a) the unprocessed filament and (b) the crazed filament. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

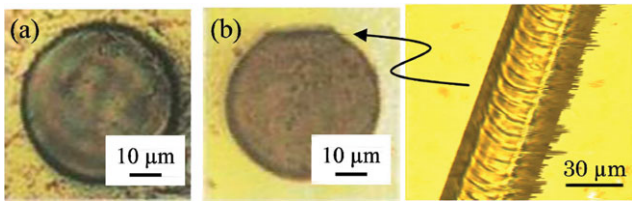

Figure 3. Optical micrographs of the cross sections of (a) the unprocessed PP filament and (b) the crazed filament. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

crazed surface and cross-section of a filament, respectively. As can be seen in Figure 3(b), there are periodic vertical dark lines in the filament structure. When a crazed filament sample is observed with transmitted light in an optical microscope, the transmitted light from the craze layer is selectively scattered and the crazes are observed as black stripes. Applying local pressure or tension on the filament will cause three types of deformations in the filament: shear, partial crack, and craze. Since all the three deformations are constantly generated, it is difficult to distinguish them from each other. In this article, the craze structure is defined in a broad sense by assuming that the lines observed in the cross-section of the fibers are crazes. As can be seen in Figure 3, there is a flat portion in the circle showing the filament cross-section; here, the shape of the unprocessed filament cross-section is assumed to be circular. The images of the filament cross-sections in Figure 3(a, b) show that the periodic structure is a result of the contact between the processing blade and the surface of the filament in the crazed area. The rate of craze lines on this flat portion is the same as that calculated from the measured width and depth of the crazes. When the blade hits the filament surface, the surface of the filament is deformed and periodic crazes are generated. Unstable necking during fiber spinning is known as a self-oscillation.[13,17–19] To investigate the changes in the internal structure of the filaments resulting from the crazing process, the filaments were photographed by a LSM (Figure 4). The results of the observations of the surface and internal structure of the filaments showed that the crazing process influenced the internal structure of the filaments, and the process led to the internal structure of the crazed filaments becoming periodic (Figure 4). In this figure, the white line at the center of the photographs of the filament before and after crazing appears because of the cylindrical shape of the filaments that leads to light being focused at the center; this white line is not a result of the crazing process. The results of observation of the illuminated crazed PP filament show that the crazed filament scatters the incident light (Figure 5). The scattering of light observed in the optical micrograph of the crazed filament suggests that pores could have been formed in the internal structure of the crazed filament and that the filament could have been spongy in its interior. Figure 6 shows the crazing process did not alter the strength of the filament, approximately. A significant shift was the breaking strain decrease in the rate of 0.47 in comparison with that before crazing. That is because of crazed filaments bending at the blade, extremely. After crazing, the Young's modulus was increased slightly. The extension of the crazed fiber was not observed after the crazing except the processing error which was the filament stacking or locking at the blade. However it was considered that the crazed fibers had the localized or limited molecular orientation in relation to the bending at the blade, because S—S curves after the crazing were similar to that of drawn PP fibers. In the other hands, it is notable that the strength of drawn fibers was increased with the increasing of the draw ratios as a matter of course; however that of the crazed fiber was almost the same as the original PP fibers. The dramatic cracks such as in Figure 5 could induce the decrease in the strength clearly. After the annealing treatment at 100°C for the confirmatory check, crazed regions disappeared under the optical microscope images.[20] It was concluded that crazes were generated mainly. By observing the surface and internal structure of the crazed filaments with an optical microscope using transmitted light, some parameters of the periodic structure of the crazed filaments, such as the

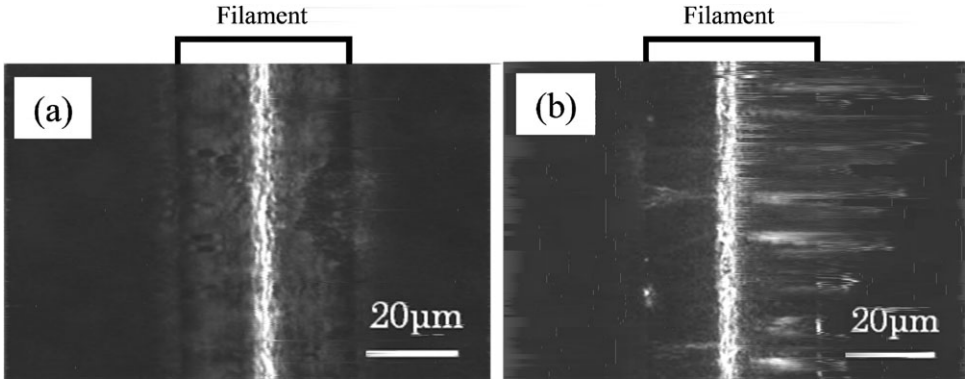

Figure 4. LSM micrographs of the PP filament: (a) The unprocessed filament and (b) the crazed filament. (Crazing stress: 6.0 MPa).

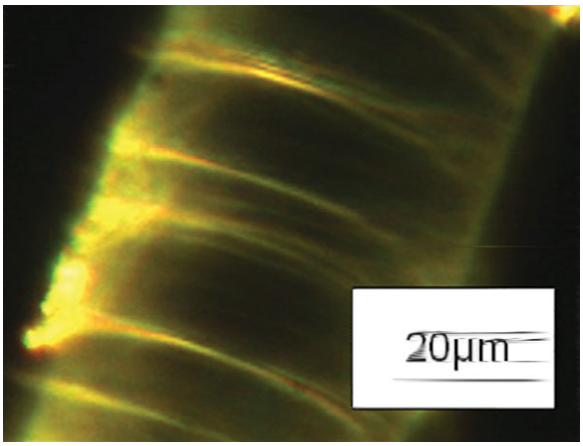

Figure 5. Optical micrograph of the illuminated crazed PP filament. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interval between the crazes and the width of the crazes, were measured from photographs. Figure 7 shows a typical schematic of this type of observation. The width of the crazes and the interval between the crazes were measured from these figures.

To determine the ratios of the crazes of the filament, 25 filaments were randomly selected, and the interval between the crazes and width of the crazes were measured at 200 points. By using the measured values, the ratios of the crazes of the filament were determined using the following equation:

$$\text{Craze ratio} = \frac{\text{Total width of the crazes}}{\text{Length of the crazed filament}} \times 100 \qquad (1)$$

The calculations performed simply by using eq. (1) show that about 30–50% of the contact area between the blade and filament was crazed. The craze ratio was estimated optically. The craze ratio is not the ratio of craze phase to total length because the craze including voids has a lower density than the original material. The density measurement had the interference of a liquid penetrant in the craze as a typical density measuring in the various liquids.

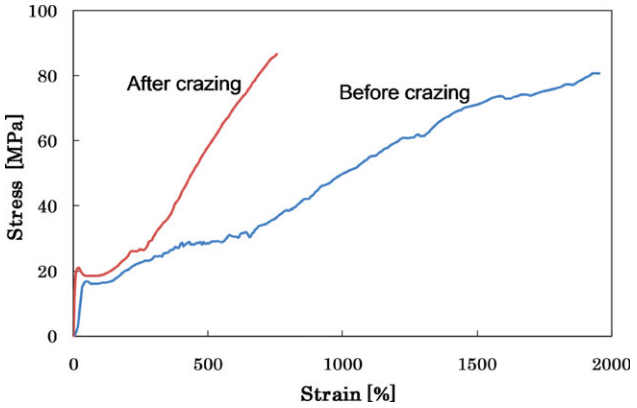

Figure 6. Stress–strain curves of the PP filament: (a) The unprocessed filament and (b) the crazed filament. (Crazing stress: 6.0 MPa). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

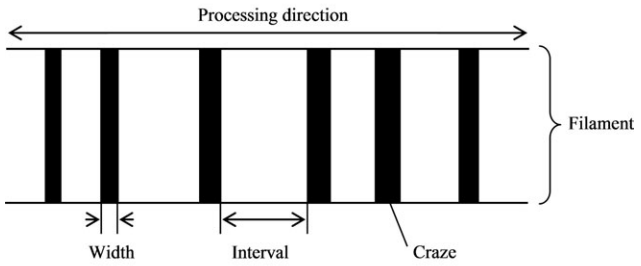

Figure 7. Schematic diagram of the craze morphology.

The effects of crazing stress on the structural parameters of the crazed filaments are shown in Figure 8. As can be seen, the crazing stress did not have a significant effect on the craze width. The diameter of the filaments after crazing was the same as that before crazing. The craze width and the crazing stress are independent of each other, mostly, because the stress concentration at the blade is released in short order after the crazing due to the fact of lower Young's modulus in the craze region. The craze at a constant width could be observed on the crazing condition above a minimum crazing stress for the filament and a fast craze growing in relation to the processing rate. However, the interval between the crazes increased from 5 μm to 9 μm when the crazing stress increased with an increase in the stress from 1.6 MPa to 10.2 MPa. The depth profiling of the crazes on the filament was

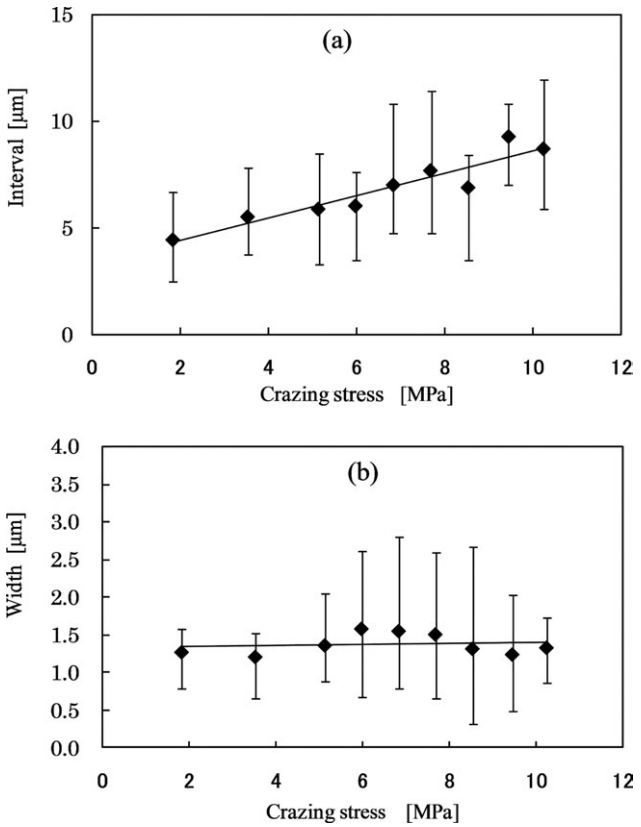

Figure 8. Effect of axial tension on the structural parameters of the crazes: (a) The effect of crazing tension on the interval between the crazes and (b) the effect of crazing tension on the width of the crazes.

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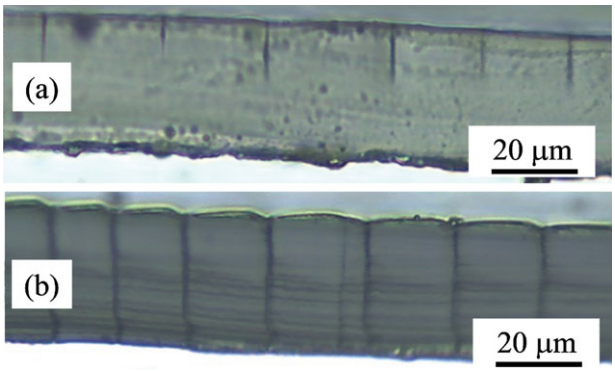

Figure 9. Optical micrographs of cross section of crazed PP film: (a) at 2 N/cm and (b) at 5 N/cm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

difficult to perform by an optical technique. However, the increase in the depth of the crazes might be related to the interval and width. The histogram of craze widths, which is the same as that of the interval between the crazes, shows that these structural parameters of the crazes on the filaments are similar to a bell curve. In fact, the depth profile of a crazed PP film could be observed (Figure 9), and the depth of the craze in the film increased with the crazing tension increasing. The interval between the crazes and the width of the crazes are approximately normally distributed along the filament length. This periodicity of crazing suggests "stick-slip" due to dynamic and static friction on the surface of the filament; this observation is in contrast to those in our previous studies.[21] Table II lists the width and interval values of the crazed PP film for comparison. The interval decreased and the width increased as the crazing stress increased. These tendencies were commonly observed for various types of PP films. The mechanism of the crazed film would be explained a three-point bending process. Moreover, the distribution of the crazes in the film corresponded to a homogeneous and periodic crazed structure and resulted in anisotropic light scattering, which gave rise to the functionality of view field selection, similar to that in the case of a privacy filter.[14,21]

Optical Light Scattering by the Crazed Filaments

To evaluate the optical anisotropy of the crazed filaments, an ultraviolet–visible light spectrometer was used to measure the visual light range in which the optical anisotropy of the crazed filaments can be observed.

In polymeric fibers, the use of solvents and surface treatment and the presence of various environmental agents can strongly affect the transparency of the fibers and sometimes those effects show their opalescence.[22] The transmittance of the crazed filaments was measured with light radiation of various wavelengths that was incident on the samples at various angles in the range −60 to 60°. The results of evaluation showed that the transmittance of the filaments had significantly decreased because of the crazing process (Table III). In comparison to unprocessed filaments, the transmittance of the crazed filaments was maximum for radiation incident at 0°, and a smooth mount-type graph was obtained for the transmittance as the incident angle varied in the range −60 to 60°. The same mount-type graph was obtained from the measurement of the transmittance of the films having optical anisotropy; however, the scattering of light indicated that there was no significant decrease in the transmittance of the crazed filaments. This was because of an increase in the reflection of light from the surface of the samples. In the

Table II. Craze Morphology of PP Films

Stress (MPa)	Width (μm)	Interval (μm)
24.5	7.0	6.2
22.1	6.5	8.0
19.6	4.0	9.7
17.2	3.1	12.0
14.7	2.6	13.2

Bending angle: 120°; processing rate: 10 mm/min; thickness: 25 μm.

Table III. Light Transmittance of Polypropylene Filaments

	Light transmittance (%)	
Light wavelength (nm)	Unprocessed	Crazed
700	32.9	18.6
600	33	18.9
500	33.1	19.3
400	33.3	19.7
300	33.3	18.8

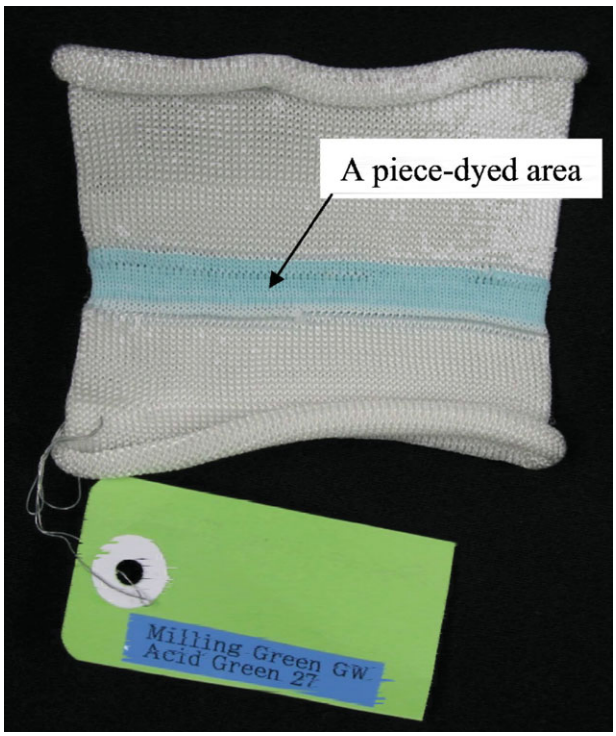

Figure 10. The crazed and normal PP fabric by a piece dying (Center blue (dark) line by C.I.Acid Green 27/Kayanol Milling Green GW) after cleaning process (rinse water: 80°, 30 min with sodium carbonate 0.05%. and cationic surfactant 0.2%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

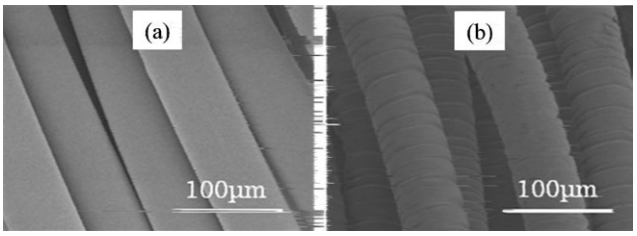

Figure 11. SEM images of the normal PP filaments (left) and the crazed PP filaments (right).

case of the crazed filaments, it was not possible to determine the transmittance of the crazed filament because the surface of each filament scattered the incident light.

Composition of the Crazed Filaments

The pores formed in the interior of the crazed filaments during the deformation by the crazing process provided easy access to the interior of the filaments; moreover, it was possible to determine the composition of the various functional materials of the filaments. For example, it is known that piece dyeing of PP filaments is very difficult, except with specific techniques, because the surface free energy of PP is very low (i.e., wettability is also low). The knitted fabric shown in Figure 10 consisted of three areas: normal PP fabric, crazed PP fabric, and normal PP fabric. Figure 11 shows the SEM images of the crazed PP filament used for manufacturing industrial products. The normal PP filaments were crazed by the technique described above and PP filaments were the same as Table I. The dyed blue line (center, dark) corresponds to the crazed filament area on the condition of 60°C and 30 min in an aqueous solution of 0.1%. The acid dyeing was adsorbed into voids in crazed region of PP filaments. It is worth noting that the dye used in the stained crazed area was not eluted after the typical cleaning process carried out in hot water (0.2% of a cationic surfactant and 0.05% of sodium carbonate, 80°C, 30 min), because the pore was closed after the dyeing. Craze regions were decreased by the thermal relaxation above 60°C. After the annealing of 80°C and 30 min, the pore disappeared and the dye was enclosed in the fiber. The dyeing in the craze was mixed physically like a melt mixing. The acid dye was chosen in this study for dyeing of PP filaments on the grounds of the compatibility with the surface free energy of PP. This lower dyeing temperature below the melting point is an interesting fact for the thermally unstable mater.

CONCLUSIONS

We designed and fabricated an experimental apparatus for generating periodic and homogeneous crazes on the PP filaments. The filaments were regularly and periodically crazed and their properties were examined. The results of the observations with optical microscopes and measurements of some of the parameters of the periodic structure of the crazes in the filaments showed that about 30–50% of the contact area between the blade and filament surface was crazed. While the interval between the crazes increased with the crazing tension, the width of the crazes did not vary significantly when the crazing tension increased. The results obtained in this study showed that the generated crazes were distributed approximately normally along the filament length, giving rise to a homogenous and periodic crazed structure. It was also concluded that the crazed filaments had a periodic internal structure and pores were formed in their interior. These crazes in the filaments have the potential to lead to new methods for dyeing PP fibers or composites of valuable molecules which were included thermally unstable species, enzyme, and medicine. These crazing method have advantages of high durability like a kneading process and a low-cost like a post-processing.

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