Influence of Heat-Stabilization on Supermolecular Structure of Colored PP Fibers

JAN BRODA, CZESŁAW ŚLUSARCZYK, ANDRZEJ WŁOCHOWICZ

Textile Institute, Technical University of Łódź, Branch in Bielsko-Biała, Poland

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ABSTRACT: Investigations of supermolecular structure and tensile properties of colored heat-stabilized fibers were carried out. For fiber coloring, chosen organic pigments with differentiated nucleating properties were used. It was stated that during the fiber formation, a fibrillar-lamellar structure with α -crystals is formed. In fibers colored with a quinacridone pigment, the minimal number of β -crystals was observed. During heat-stabilization, perfecting of the supermolecular structure of the fiber occurs. Because of pigments, the process of rebuilding occurs more intensively and leads to formation of a more stable structure with higher crystallinity. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 477-488, 1999

Key words: polypropylene fiber; fiber structure; pigment; heat-stabilization; nucleation

INTRODUCTION

During the heat-stabilization the rebuilding of the supermolecular structure of the fiber, occurs. The changes aim at better arrangement of macromolecules and at forming a more perfect and stable structure. During the stabilization, the arrangement of macromolecules in less orderly parts is observed. In crystalline parts, elimination of defects and perfection of the crystal lattice take place. Simultaneously, through including new macromolecules into the crystal lattice, the increases of crystallite size and fiber crystallinity are observed.

In polypropylene (PP) fibers, the supermolecular structure undergoes strong differentiation. Depending on the forming conditions and material parameters, a mesophase structure or a partly crystalline structure¹ is formed.

For PP, the following three polymorphic forms are known: monoclinic α -form, hexagonal β -form, and triclinic γ -form.² Usually, the most stable α -form is found in fibers. During heat-stabilization of fibers, a recrystallization process occurs, which leads to the enlargement of α -crystals and to increasing their perfection. In some cases, in fibers, β modification³ appears. The β -form does not appear individually but together with the α -form. During heating, the crystallite recrystallization of β -form may proceed in two directions, as $\beta\beta$ recrystallization or $\beta\alpha^4$ recrystallization. The $\beta\alpha$ recrystallization occurs within the β -form and leads to β -form structure perfection. The $\beta \alpha$ recrystallization is connected with the polymorphous transformation $\beta \rightarrow \alpha$.⁵ The polymorphous transformation $\beta \rightarrow \alpha$ takes place when the crystallized structure has been cooled below the critical temperature $T_R = 100$ °C.

The mesophase structure, called smectic or paracrystalline, is characterized by partial ordering of macromolecules. During heating above 70°C, the mesophase structure changes into α -form.⁶ Rate of conversion is the function of time and temperature.

Correspondence to: A. Wlochowicz.

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In colored fibers, the described changes take place with the presence of pigments. The pigments belong to active nucleants and strongly influence the course of PP crystallization.⁷

This article shows the results of research relating to participation of pigments in changing supermolecular structure of PP fibers, which occurs during heat-stabilization.

EXPERIMENTAL

Samples

The investigation was carried out for PP fibers formed in laboratory conditions by means of a Brabender extruder. Shell isotactic PP was used with the melt flow index 30 g/10 min.

Fibers were extruded from the melt with a temperature of 250°C to the air temperature of 20°C. A five-hole spinneret with a diameter of ϕ = 0.2 mm was used. Fibers were spun with a take-up velocity of 1350 m/min.

For fiber colouring, the chosen organic pigments used were Blue pigment B (Wola Krzysztoporska), Echtrot E3B, and Echtrot HF4B (Hoechst) and their 40% masterbatches were as follows: Remafin Rot E3B and Remafin Rot HF4B. The pigment Echtrot E3B is a quinacridone pigment and Echtrot HF4B is an azo pigment, whereas Blue pigment is a phtalocyanine pigment. The chemical formulas of used pigments are presented in Table I.

The applied pigments have different abilities in the nucleation of PP crystallization. The phtalocyanine pigment is known as a good nucleator of the α -form,⁸ whereas the quinacridone pigment as one of the best nucleators of the β -form.⁹

The pigments and masterbatches were mixed with a polymer granulate immediately before forming fibers in the amount of 0.5% to the polymer mass. The fibers were submitted to the heat-treatment in a "not tensed" state for 3 min in hot air with temperatures of 120, 130, 140, 150, and 160°C.

Measurement Methods

The wide-angle X-ray scattering (WAXS) investigation was carried out with an X-ray diffractometer HZG-4. The diffraction pattern was registered for the powder samples in angular range of 5–35°. The diffraction pattern analysis was carried out using the Hindeleh–Johnson method,¹⁰

Table IChemical Formulas of the UsedPigments



constructing a theoretical curve consisting of crystalline peaks, an amorphous peak, and a background scattering. On the basis of the received patterns, a crystallinity index, the width of peak at half-maximum $(110)_{\alpha}$, and the K-value for the fibers containing β -form were calculated. The crystallinity index was determined as ratio of the area under crystalline peaks to the total area. The K-value was determined according to the proposition of Turner–Jones et al.¹¹ on the basis of formula (1), as follows:

$$K = \frac{I(300)_{\beta}}{I(300)_{\beta} + I(110)_{\alpha} + I(040)_{\alpha} + I(130)_{\alpha}} \quad (1)$$

The small-angle X-ray scattering (SAXS) investigations were performed by means of a MBraun (Austria) SWAX camera, which utilizes conventional Kratky collimation system. The front of the camera was directly mounted on the top of the tube shield of a stabilized Philips PW 1830 X-ray generator. The experimental SAXS curves were corrected for sample absorption and desmeared



Figure 1 Effect of pigments on WAXS patterns of fibers before stabilization: (1) undyed; (2) Phtalocyanine Blue; (3) Echt Rot HF4B; (4) Echt Rot E3B.

from collimation distortions by means of the computer program 3DVIEW supplied by MBraun. The calorimetric investigation was carried out with a DuPont scanning calorimeter with the linear function of temperature increase. The samples of fibers were heated at a rate of 10 K/min from 293 to 473 K. The thermograms were presented in a standard arrangement, illustrating the power effect of melting transformation in the function of sample temperature. The heat of melting, the temperature of melting, and the temperature of the extreme of power effect in a melting process were calculated by means of the program General V4, 1C DuPont, 2100. The temperature of transformation was determined with the standard method as the intersection point of tangent to the front of heat in the point of inflection with the basic line. Investigation of tensile properties was carried out by means of Instron tensile testing machine. The samples of initial length of 10 mm were stretched with speed of 100 mm/min. On the basis of stress-strain curves, tenacity and break elongation were calculated. The received values are the mean of 30 measurements.

The microscope observations of fibers were carried out with electron scanning microscope JSM-15 Jeol equipped with a wolfram source of electrons. Fiber preparations were glued with conductive glue to carrying stands and evaporated with a layer of gold and silver.

RESULTS

Wide-Angle X-Ray Scattering

For colorless fibers and fibers colored with pigments Echt Rot HFT4B and Blue pigment, X-ray diffraction (XRD) patterns characteristic for the PP α -form were obtained (Fig. 1).

The received patterns show that the structure created during the fiber formation is partly crystalline and includes well-formed α -crystals. The intensity of peaks (110), (040), and (130) is similar to the intensity of peaks (111) and (041). For stabilized fibers with temperature growth, the intensity of peaks (hk0) increases (Fig. 2). The change in the intensity of peaks causes the change in the proportion of peak intensity. For stabilized fibers, the intensity of peaks (111) and (041). For colored fibers, together with the increase of intensity, peaks (hk0) become narrower. The observed changes prove that the crystal structure is perfected.

For colorless fibers stabilized in 160°C, the intensity of peaks decreases. The observed decrease in intensity of peaks is caused by the beginning of melting. For fibers containing pigments stabilized in the same temperature, similar changes were not observed. The pattern has very well-formed peaks without signs of beginning melting. For fibers colored with pigment Echt Rot E3B, peak (300) from the β -form is seen on the pattern, together with characteristic α -form peaks. The intensity of peak $(300)_{\beta}$ is not great, which indicates a low content of the β -crystal. The K-value for fibers is 0.06. The weak peak (300) of the β -form with a similar intensity was observed both for fibers colored with masterbatch and for pure pigment.

Pigment Echt Rot E3B is a very effective nucleating agent of the β -form. By proper selection



Figure 2 WAXS patterns of the fibers dyed with Phtalocyanine Blue: (1) unstabilized, and stabilized at (2) 120, (3) 140, and (4) 160°C.



Figure 3 Effect of heat-stabilization on the crystallinity index of fibers: (1) undyed; (2) Phtalocyanine Blue; (3) Echt Rot E3B.

of pigment concentration and crystallization parameters, the content of the β -form can be very high, and the K-value may reach 0.6-0.8¹² A much lower content of the β -crystal in formed fibers is caused by the following two factors: high temperature of extruded polymer melt and orientation. The tested fibers were formed from the melt with high temperature of 250°C, with a high take-up velocity of 1350 m/min. When the temperature of melted polymer increases, the content of the β -form decreases. When the melt temperature exceeds 260°C, then the β -crystal does not develop in spite of a great content of nucleator.¹³ In fiber-forming conditions, the solidifying polymer melt is submitted to strong orientation. Under the orientation polymer, crystallization occurs much faster on row nuclei. In these conditions, the nucleation influence of pigments is very limited.

For stabilized fibers, peak $(300)_{\beta}$ is seen for fibers treated in temperatures of 120, 130, and 140°C. The participation of the β -crystal, characterized by the K-value, does not change and equals 0.06. For fibers stabilized in 150 and 160°C, the peak $(300)_{\beta}$ disappears. The peak disappearing is caused by transformation $\beta \rightarrow \alpha$. The temperature of observed transformation is between 140–150°C, which corresponds well with the results of other authors.^{14–16}

The crystallinity index for all not stabilized fibers has the same value of 0.47-0.51. Similar

values of crystallinity index were received, irrespective of pigment content also for fibers containing the β -form. For stabilized fibers, the crystallinity index increases and grows, together with the increase of stabilization temperature to 140°C (Fig. 3).

For fibers stabilized in higher temperatures of 150 and 160°C, the crystallinity index does not increase and is the same with the value for fibers stabilized in temperature 140°C.

The observed changes of crystallinity index are higher for fibers with pigments. Irrespective of added pigment, for all stabilized and colored fibers, values of crystallinity index are about 10% higher compared to colourless fibers.

The peak width at half-maximum $(110)_{\alpha}$ for fibers not stabilized takes values from 0.9-1.4. Fibers not colored, stabilized in various temperature peak widths at half-maximum $(110)_{\alpha}$, are arranged irregularly between 1.2-1.4. For colored fibers peak width at half-maximum $(110)_{\alpha}$ decreases during stabilization (Fig. 4). A systematic decrease of peak width at half-maximum $(110)_{\alpha}$ occurs with an increase of the stabilization temperature. A similar nature of changes is observed for all colored fibers. Decreasing the peak width at half-maximum can be interpreted as an increase in crystal perfection and/or crystallite size.¹⁷

Small-Angle X-Ray Scattering

Figure 5 presents SAXS curves for colorless fibers stabilized in various temperatures. These curves



Figure 4 Effect of heat-stabilization on the width at half-maximum of the (110) peak: (1) undyed; (2) Phtalocyanine Blue; (3) Echt Rot E3B.

exhibit a distinct maximum, which is connected with the lamellar structure of PP.¹⁸ The long period L of this structure (obtained from Bragg's law) corresponds to the maximum varies from 11.2 to 10.9 nm for the fibers not stabilized and stabilized in 160°C, respectively. The intensity of the maximum changes, depending on stabilization temperature. The highest intensity one can observe is for fibers stabilized in 140°C and the lowest is for the sample stabilized in 160°C. The change of SAXS maximum intensity is closely related to the change of the electron density contrast (i.e., the electron density difference) between crystalline and amorphous regions in the sample. Thus, the increase of scattering intensity may be interpreted in terms of improvement of the lamellar structure in fibers stabilized in temperatures less than 140°C. Similarly, the decrease of scattering intensity for the fibers stabilized in 160°C can indicate that the lamellar structure begins to disappear, although the crystalline phase still exists in these fibers. Such observations are in good agreement with the results obtained by the WAXS method.

The use of the correlation function calculated from the SAXS curve enables a more accurate characterization of the lamellar structure. A typical pattern for this function obtained for one of the samples studied is shown in Figure 6. Vonk and Pijpers,¹⁹ as well as Strobl and coworkers,²⁰ have shown that this function can be a source of information concerning the long period L and the average value of the thickness $\langle l_c \rangle$ of the crystal-line layers in lamellar stacks. Figure 6 shows how these parameters can be estimated from the correlation function.

SAXS measurements reveal that for colorless fibers, heat-stabilization causes small changes in the values of a long period and other structural



Figure 5 SAXS curves for undyed fibers: (1) unstabilized, and stabilized at (2) 120, (3) 140, and (4) 160°C.



Figure 6 The correlation function for fibers colored with Phtalocyanine Blue and stabilized at 160°C.

parameters (Fig. 7). The changes of these parameters for colored fibers are more distinct. SAXS patterns for these fibers are shown in Figures 8 and 9. In contrast to colourless fibers, the intensity of SAXS maximum systematically increases for both types of colored fibers as the stabilization temperature increases. The long period varies from 11 to 12.2 nm for fibers colored with Echt Rot E3B and from 10.8 to 13.1 nm for fibers colored with blue pigment (Fig. 7). It can indicate that the presence of pigments, during the heatstabilization process, enhances a process of improvement of a lamellar structure of the fibers. For colored fibers, the lamellar structure is more stable.

Differential Scanning Calorimetry

In the course of differential scanning calorimetry (DSC) investigation, a thermogram with one endothermic peak, which corresponds with melting process of α -crystals, was received.²¹ The similar shape of the thermogram was obtained for all tested fibers with the β -crystal. Missing of the second peak characteristic for the β -form is caused by very a low content of this form in the fiber.

For fibers not stabilized, the maximum of the colored fiber peak is 2 K higher than the maximum of colorless fibers (Fig. 10). Resulting from stabilization, the position of peak maximum moves towards higher temperatures. For fibers stabilized in 140°C, it reaches values of about 2 K higher than values obtained for fibers not stabilized (Fig. 11). For fibers stabilized in 160°C, the peak maximum moves in the opposite direction

and occupies a position close to the position of the peak for fibers not stabilized.

For all fibers not stabilized, the energy of transformation accepts the same values. For stabilized fibers, the energy of transformation increases, together with an increase of the stabilization temperature up to 140°C. For fibers stabilized in 160°C, the energy of transformation decreases and accepts values lower than values obtained for fibers not stabilized. The highest decrease of transformation energy was recorded for colorless fibers. The course of changes in values marked on the basis of thermograms corresponds well with the results obtained on the basis of WAXS experiments.



Figure 7 Effect of heat-stabilization on (a) the long period of fibers and (b) the thickness of the crystalline layer of fibers: (1) undyed; (2) Echt Rot E3B; (3) Phtalocyanine Blue.



Figure 8 SAXS curves for fibers colored with Echt Rot E3B: (1) unstabilized, and stabilized at (2) 120, (3) 140, and (4) 160°C.

Tensile Properties

For all fibers, the same stress-strain curve was obtained. Irrespective of the presence of pigments

and stabilization temperature, the stress-strain curve increases gradually up to the fiber fracture (Fig. 12). Tenacity of fibers not stabilized is 1.2-



Figure 9 SAXS curves for fibers colored with Phtalocyanine Blue: (1) unstabilized, and stabilized at (2) 120, (3) 140, and (4) 160°C.



Figure 10 Thermogram DSC of the unstabilized fibers: (1) undyed; (2) Echt Rot E3B; (3) Phtalocyanine Blue.

2.0 cN/dtex. All fibers containing pigments have lower tenacity in comparison with colourless fibers. For fibers coloured with pigment Echtrot HF4B, obtained values are lower about 0.2 cN/ dtex. For fibers coloured with Blue pigment, they are lower about 0.3 cN/dtex. The lowest tenacity, lower than about 0.6 cN/dtex, was obtained for fibers containing pigment Echtrot E3B and its masterbatch Remafin Rot E3B. As it was found on the basis of WAXS investigation, fibers coloured with this pigment contain a small content of the β -crystal. Lower tenacity of these fibers is connected with the presence of this form.²²

For stabilized fibers, tenacity increases gradually with the stabilization temperature up to 150°C (Fig. 13). For fibers stabilized at 160°C, the tenacity of fibers drops and is lower than the tenacity of fibers not stabilized. The tenacity drop is caused by the beginning of melting. For colorless fibers not stabilized, a great spread of measured values was observed. It was caused by great irregularity of fibers. Coloured fibers are uniform so that the standard deviation of measured values is two times smaller. For stabilized fibers, the properties of particular fibers equalize, and the standard deviation obtains values that are the same for all fibers. Break elongation for all fibers not stabilized is between 420-600%. High elongation values result from the fact that tested fibers were not subjected to an isolated process of stretching. Elongation for fibers with pigment Echtrot E3B obtains lower values; for fibers with Echtrot HF4B, it obtains approximate values; and for fibers coloured with blue pigment, elongation obtains higher values than for colorless fibers.

For fibers stabilized with increase of stabilization temperature, the break elongation of fibers decreases gradually (Fig. 14). A similar tendency was observed for all fibers irrespective of pigment content. Break elongation depends on the energy of interfibrillar cohesion. Under the influence of heat-stabilization, the energy of interfibrillar cohesion improved. The observed smaller break elongation of stabilized fibers is the result of the improved interfibrillar cohesion.²³

Electron Microscopy

During microscopic research, observations of fiber surface and fractures were carried out. The observations were carried out with enlargements from 200–2000 times.

The research showed that the surface of fibers is smooth, without any slits and roughness [Fig. 15(a)]. Small particles of pigments can be noticed



Figure 11 Thermogram of the undyed fibers: (1) unstabilized, and stabilized at (2) 140, and (3) 160°C.

for fibers colored on the surface. A smooth surface is found for all tested fibers, stabilized and not stabilized.

The significant differences between colored fibers and ones not colored were found in the picture of fiber fractures [Fig. 15(b)]. For colorless fibers, the fracture has an elasticly viscoelastic

character.²⁴ A well-formed fibrillar structure is seen on the fracture. On the surface of fiber, there are longitudinal crazes and slots separating particular fibrils. For coloured fibers on the fracture, there are numerous slots perpendicular to the axis. A similar picture was observed for all coloured fibers, stabilized or not stabilized, irrespective of pigment.



Figure 12 Stress-strain characteristic for the fibers dyed with Phtalocyanine Blue: (1) unstabilized, and stabilized at (2) 120, (3) 130, (4) 140, (5) 150, (6) 160°C.



Figure 13 Effect of pigments on tenacity of fibers: (1) undyed; (2) Phtalocyanine Blue; (3) Echt Rot HF4B; (4) Echt Rot E3B.



Figure 14 Effect of pigments on the break elongation of fibers: (1) undyed; (2) Phtalocyanine Blue; (3) Echt Rot HF4B; (4) Echt Rot E3B.

DISCUSSION

During fiber formation, a partly crystalline, fibrillar–lamellar structure is formed. Inside fibrils, the lamellar crystallites are aligned alternatingly with amorphous phase. In all tested fibers, α -crystals are formed. In fibers containing Echt Rot E3B pigment, some β -crystals are created. In spite of high nucleating capacities of this pigment, the β content is not great. Because of pigments, the formed structure is more stable with less defects.

In the time of fiber formation, pigments that are in the melt of crystallized polymer are forced outside growing crystals. Particles of aggregated pigments with dimensions comparable to thickness of fibrils locate in interfibrillar zones.²⁵ During fiber drawing, the fibrillization process occurs. It leads to distinct separation of fibrils. Because of the low interfibrillar cohesion, which results from a small amount of connecting macromolecules and from weak interfibrillar bonding, the fibrillization process of PP fibers proceeds easily. In the time of fibrillization, neighboring fibrils slide past one another and leave vacancies behind them.

Under the influence of the localized stresses caused by defects, voids will stretch perpendicularly to the fiber axis, separating bundles of fibrils. An irregular net with crazes appears on the fiber surface.²⁶ A craze can be defined as a zone spanned by aligned fibrils alternating with elongated voids, both being parallel to the draw axis.²³ The occurring deformation takes the capacity of all fibers across the fiber diameter and increases with an increase in elongation. Lateral crazes become higher and higher, until fiber breaks. Pigments that are located in interfibrillar zones disturb in the reciprocal displacement of fibrils. Numerous places with localized stresses are formed with the presence of pigments. In the result, numerous lateral slots are formed with the presence of pigments, which leads to a decreased strength of fiber.

During the heat stabilization, the rebuilding of the fiber supermolecular structure occurs. The observed changes lead to better alignment of macromolecules. The process of eliminating defects leads to perfecting the crystal net. Simultaneously, through including macromolecules in the crystal lattice, the size of crystals perpendicular to fiber axis grow, and the crystallinity of the fiber increases. As the result of occurring changes, the interfibrillar cohesion increases.

The range of observed changes depends on the stabilization temperature. The changes are higher and higher with the increase of stabilization temperature from 120 to 140°C. Resulting from stabilization in 150°C, the obtained effects are close to effects obtained in 140°C. During stabilization in 160°C, the process of decomposition of fiber structure begins. Treatment in this temperature causes substantial changes of structural parameters and deterioration of tensile properties for colorless fibers. The structure of colored fibers is more stable. The diffraction picture of fibers does not show signs of decomposition, and the calculated structural parameters are identical with the parameters obtained for fibers stabilized in 150°C.

Pigments promote perfecting fiber structure. In the presence of pigments, rebuilding of structure is more intensive, and the range of observed changes is greater than for colorless fibers. Comparable changes of structural parameters for colored fibers occur in the lower stabilization temperature. In the presence of pigments, a more stable structure is created with higher crystallinity. A similar pigment influence in the same range was observed for all colored fibers. The same changes were obtained, irrespective of the kind and form of pigment. The minimal number of β -crystals is formed for fibers with Echtrot E3B during formation. During the stabilization to 140°C, the β -form content does not change. In fibers, perfecting of α -crystals occurs, as well as other changes as fibers with remaining pigments. The polymorphous transformation $\beta \rightarrow \alpha$ occurring above 140°C, in relation to a small number of



(1)



(2)



Figure 15 Microphotographs of fibers: (1) surface of fibers dyed with Echt Rot E3B, unstabilized; (2) surface of fibers dyed with Echt Rot E3B stabilized at 160°C; (3) fracture of undyed fibers; (4) fracture of the fibers dyed with Echt Rot E3B stabilized at 120°C; (5) fracture of the fibers dyed with Echt Rot E3B stabilized at 160°C.

 β -crystals, has minimal significance and does not affect the amount of other fiber parameters.

CONCLUSIONS

During fiber formation, the influence of pigments on supermolecular structure of crystallizable polymer is much smaller than during the crystallization from quiescent melt. The addition of quinacridone pigment causes formation of the minimal amount of β -crystals. During heat-stabilization with pigments, the process of perfecting the supermolecular structure of fiber occurs more intensively and leads to the formation of a more stable structure with higher crystallinity. Because of the presence of pigment particles, colored fibers have smaller strength. Heat-stabilization of PP fiber may be carried out below 150°C. Above this temperature, the melting process begins, which leads to sudden deterioration of tensile properties. This article was financed by the Polish Committee for Scientific Research (Grant No 3T09 B10212).

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