

Formation of Polypropylene/Stearic Acid Fibers

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ABSTRACT: Polypropylene/stearic acid fibers were produced in laboratory conditions from hot homogenous blends. After formation, as-spun fibers were treated in potassium hydroxide and rinsed in water. Supermolecular structure and morphology of fibers were investigated by wide-angle X-ray scattering, FTIR, and scanning electron microscopic (SEM) methods. It was stated that by fibers' formation, thermally induced phase separation takes place. Polypropylene starts to crystallize, while liquid stearic acid is expelled out and forms drops wrapped in polymer matrix. As a result of the crystallization inside fibers the

structure with high content of mesophase is formed. During crystallization, interactions between stearic acid and polypropylene are observed. As a result of alkali treatment and rinsing, drops of stearic acid are partially removed. After removal of the stearic acid from the fibers, the porous structure is formed. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1020–1026, 2012

Key words: polypropylene fibers; stearic acid; thermal induced phase separation; crystallization; structure; morphology

INTRODUCTION

Polypropylene is known as a valuable fibre-forming polymer. Due to low density, high tensile strength, excellent chemical and biological resistance, low cost and easy processing it is broadly used in various technical and textile applications.

In some applications, properties of polypropylene fibers do not satisfy the special requirements and hence their modification is required. The modification is usually carried out by adding additives, which are incorporated into polymer by physical means during fiber formation.^{1,2} Another possibility is the application of polypropylene copolymers or polymer blends. Commonly blends of polypropylene with different polymers are used.³ In this way, improvement of mechanical properties and dyeability of fibers was achieved.

Among potential additives, fatty acids and their salts can modify properties of polypropylene fibers. Fatty acids belong to phase change materials and are used for thermal storage applications.^{4–6} Fatty acids possess long aliphatic chain and their melting point lies below the melting temperature of polypropylene. In liquid state, fatty acids are miscible with polypropylene melt and form homogenous blends.

The blends have low viscosity and can be easily extruded through orifices of the spinneret.

By formation of polypropylene/fatty acid fibers, the thermally induced phase separation occurs.⁷ At a certain temperature polypropylene starts to crystallize, while liquid fatty acid is expelled out and form drops wrapped in polymer matrix. Polymer–acid interactions influence on the polymer crystallization and consequently affect the structure of the fibers.

Current knowledge on such interactions as well as the structure of fibers extruded from polymer–diluent systems is strongly limited. At the literature of subject only one paper can be find, which reports studies on the morphology of fibers extruded from the polypropylene/liquid paraffin blend.⁸

In our studies, polypropylene blended with stearic acid was applied. The polypropylene/stearic acid fibers were produced and morphology as well supermolecular structure of fibers were investigated.

EXPERIMENTAL

Samples

Polypropylene/stearic acid fibers were obtained in laboratory conditions. Fibers were spun from hot blends of polypropylene and stearic acid. Blends with different stearic acid concentrations (5%, 10%, 15%, 20%, and 30%) were prepared.

The commercial isotactic polypropylene resin Moplen HP 462R characterized by melt flow index 25 g/10 min supplied by BASSELL (The Netherlands) and the stearic acid characterized by melting point

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67°C and density 0.87 g/cm³ supplied by POCH SA (Poland) were used.

Fibers were formed by a laboratory screw extruder coupled with a five-hole spinneret with a diameter $\phi = 0.2$ mm. The fibers were extruded from the melt at the temperature 170°C at a constant throughput rate of 3 g/min into the air at the room temperature and were taken at take-up velocity 850 m/min. The as-spun fibers were treated for 3 h in the temperature of 90°C in the 5% potassium hydroxide solution. Finally, fibers were treble rinsed in cold water.

Measuring methods

The spectroscopic investigations of fibers were carried out using Fourier transform infrared spectroscopy (FTIR) spectrometer MAGNA 860 supplied by NICOLET. Fibers were cut into 1–3 mm pieces and blended with powdered potassium bromide. The blends were pressed under 200 MPa. The tablet was placed in a measuring chamber of the spectrometer equipped with a mirror beam collimator (focused 16 \times). As a reference, the tablet made of KBr (without fibers) was used.

The supermolecular structure of the fibers was studied using the wide-angle X-ray scattering (WAXS) method. The measurements were performed with a X-ray diffractometer Seifert. The diffraction patterns were registered for the powder samples in an angular range 5° to 35°. The analysis of diffraction patterns was carried out according to the Hindele–Johnson method using WAXSFIT computer program.⁹ The crystallinity index and the mesophase content were determined.

The examinations of the fibers' morphology were carried out by means of electron microscopy. The scanning electron microscope JEOL JSM 5500 LV was used. The electron microscope was operated in backscattered electron mode. The observations were performed for samples sputtered with gold in Jeol JFC 1200 ionic sputter.

RESULTS AND DISCUSSION

As a result of the extrusion, the polypropylene/stearic acid fibers were obtained. On the FTIR spectra for as-spun fibers besides typical polypropylene bands, bands characteristic for stearic acid are observed (Fig. 1).

On the spectra close to 1700 cm⁻¹, the intense band is well visible. The band is one of the most characteristic for carboxylic acids and corresponds with stretching of the carbonyl group. Additionally, close to 700 cm⁻¹, the splitted band is observed. The band represents methylene rocking vibration and is indicative of long-chain linear aliphatic structure of stearic acid. The absorption of the band for the polypropylene/stearic acid fibers depends on the acid

concentration. The lowest absorption is observed for fibers extruded by the lowest acid concentration of 5%. Obviously, for higher concentrations the band absorption gradually increases (Fig. 2).

For pure stearic acid, the band from the carbonyl group occurs at 1696 cm⁻¹. For polypropylene/stearic acid fibers, the position of the C=O band moves toward higher energies (Fig. 3).

It is known that the position of the C=O band is strongly influenced by hydrogen bonding. Molecule of carboxylic acids contains one hydroxyl group apart from carbonyl group. As a result of the interaction between those groups, a stable dimeric hydrogen-bonded structure is formed. The hydrogen bonds are so strong that the acid molecules are bound together in dimers in solid and liquid state. Monomer form occurs only in gaseous state and in dilute solution.

The shifting of the C=O band for polypropylene/stearic acid fibers indicates the weakening of hydrogen bonds between stearic acid molecules and at least partial disintegration of the stearic acid dimers.

By fibers' formation, the extruded filament, which leaves orifices of the spinning nozzle, is intensively cooled. Cooling of the polypropylene/stearic acid blend induces the phase separation. The melting temperature of stearic acid equals to 70°C.¹⁰ Usually the crystallization temperature of polypropylene is much higher. Even by homogenous nucleation of the quiescent melt of polypropylene, the temperature of crystallization considerably exceeds 100°C.¹¹ It is considerably above the melting temperature of the stearic acid, which indicates that by cooling of the polypropylene/stearic acid blend solid-liquid thermally induced phase separation occurs. Polypropylene solidifies first in higher temperature forming semicrystalline structure. Liquid stearic acid is expelled from growing polypropylene crystals and form drops wrapped in polymer matrix.

During polypropylene crystallization, the semicrystalline structure is formed. On the WAXS patterns obtained for investigated fibers, peaks typical for polypropylene are observed [(Fig. 4(a)]. Peaks characteristic for stearic acid [(Fig. 4(b))] are too weak and are not visible on the patterns for the blend fibers.

On the pattern for fibers extruded from pure polypropylene, several well separated crystalline peaks are visible. Peaks correspond with the monoclinic α form, the most stable and the most often encountered polymorphic form of polypropylene.¹² On patterns of fibers extruded from the polypropylene/stearic acid blends, less distinguished peaks are observed. For lower stearic acid concentration, the crystalline peaks are overlapped by two broader mesophase peaks. With the increase of the acid concentration, the intensity of the mesophase peaks

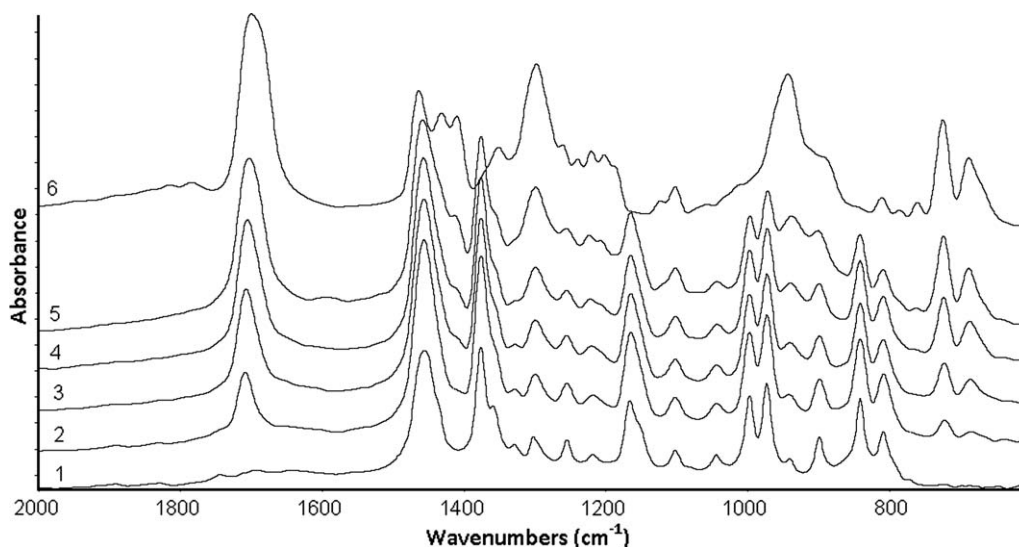


Figure 1 FTIR spectra for: 1/pure polypropylene fibers; 2/polypropylene/stearic acid fiber (5% of stearic acid); 3/polypropylene/stearic acid fiber (10% of stearic acid); 4/polypropylene/stearic acid fiber (15% of stearic acid); 5/polypropylene/stearic acid fiber (30% of stearic acid); 6/stearic acid.

decreases and sharper crystalline peaks become more visible.

The WAXS investigations reveal that inside fibers the structure, which contains three phases is formed. The content of particular phases (crystalline phase, mesophase, and amorphous phase) changes according to the change of stearic acid concentration (Table I).

For pure polypropylene, the fibers contain only two phases: crystalline and amorphous. The crystallinity index for this fibres equals 0.53. For fibers extruded from the polypropylene/stearic acid blend, besides crystalline and amorphous phases the meso-

phase appears. For low acid concentration (5%), mesophase content equals 0.25. For higher acid concentration (above 15%), the content of the mesophase decreases by 0.15. With the decrease in the mesophase content contribution of the crystalline part increases and for the highest stearic acid concentration it reaches 0.38.

The mesophase reveals intermediate order between amorphous and crystalline phases. Although the nature of mesophase is not fully understood, it is widely accepted that mesophase is made up of bundles of parallel chains, which maintain three-fold helical conformation typical for all

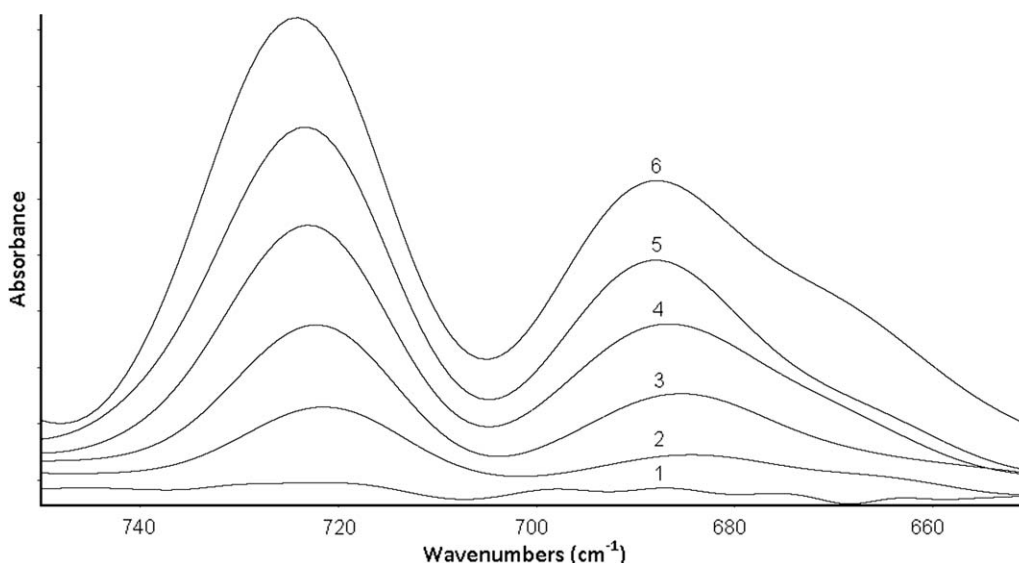


Figure 2 FTIR spectra within the range 750–650 cm^{-1} for: 1/pure polypropylene fibers; 2/polypropylene/stearic acid fiber (5% of stearic acid); 3/polypropylene/stearic acid fiber (10% of stearic acid); 4/polypropylene/stearic acid fiber (15% of stearic acid); 5/polypropylene/stearic acid fiber (30% of stearic acid); 6/stearic acid.

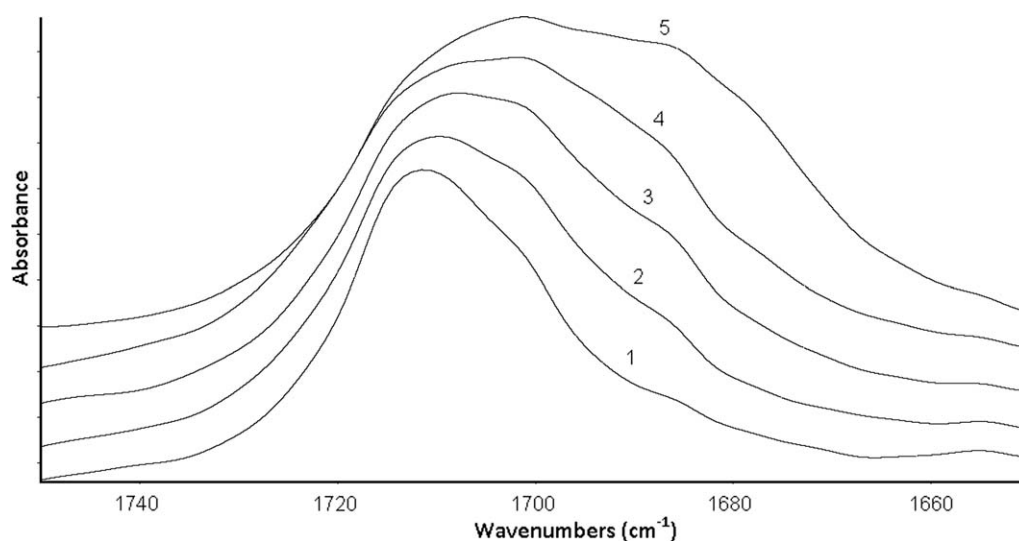


Figure 3 FTIR spectra within the range 1750–1650 cm^{-1} for: 1/polypropylene/stearic acid fiber (5% of stearic acid); 2/polypropylene/stearic acid fiber (10% of stearic acid); 3/polypropylene/stearic acid fiber (15% of stearic acid); 4/polypropylene/stearic acid fiber (30% of stearic acid); 5/stearic acid.

polymorphic forms of polypropylene. In the bundles, long-range ordering maintains only along the chain axes, whereas in lateral packing a large amount of disorder is present.¹³ Mesophase is formed by quenching of the molten polypropylene at a drastic cooling rate^{14,15} or by deformation of the crystalline structure.¹⁶

The formation of mesophase in polypropylene fibers was observed repeatedly. Many studies revealed that the content of mesophase in the fibers depends strongly on the molecular structure of polypropylene and formation parameters.^{17–20} The high content of mesophase was observed in fibers extruded from polypropylene with low molecular weight,²¹ fibers taken at low velocities,^{22–24} or fibers intensively cooled in water with addition of ice or in the mixture of dry ice and acetone.^{25–29}

The presence of the mesophase in fibers extruded from polypropylene/stearic acid blend indicates the influence of the stearic acid on the polypropylene crystallization.

The effect of stearic acid on polypropylene crystallization was reported for polypropylene composites.^{30,31} For the preparation of such composites, fillers coated with stearic acid are often applied.^{32–37} Acid molecules are coupled to the filler's surface with ionic bonds and are oriented in the directions normal to the surface. As a result, the tendency to agglomerate and the surface free energy of the filler reduce dramatically. Consequently, better dispersion of the particles in polymer matrix is achieved.

However, the modification of polypropylene with stearic acid date back to 1966,³⁸ the mechanism of interaction between the stearic acid coating and the polypropylene and its influence on the crystallization

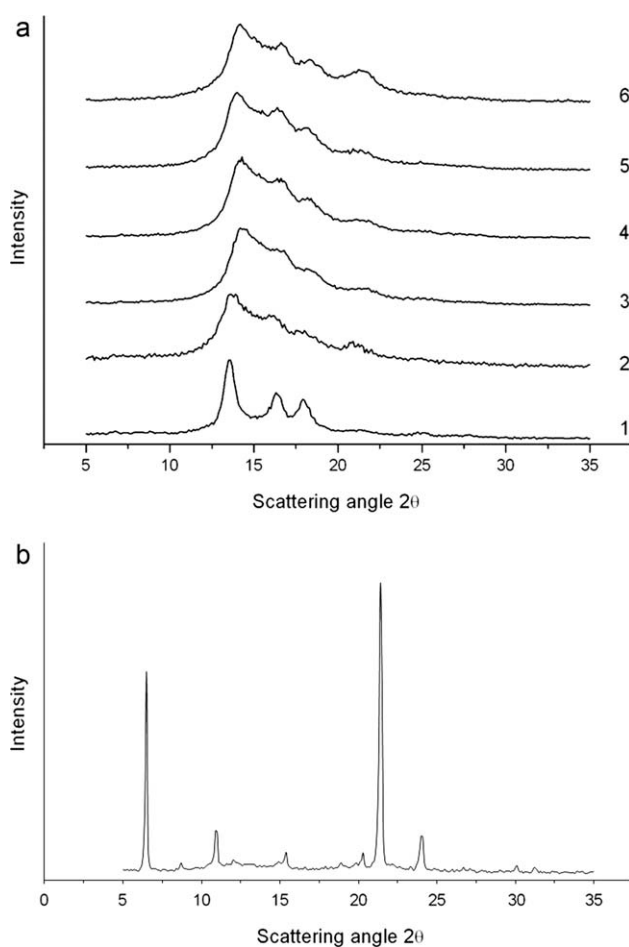


Figure 4 (a) WAXS patterns for polypropylene/stearic acid fibers extruded by different stearic acid concentrations; 1/0%; 2/5%; 3/10%; 4/15%; 5/20%; 6/30%. (b) WAXS pattern for stearic acid.

TABLE I
Structural Parameters of Polypropylene/Stearic Acid Fibers

Stearic acid concentration	Crystallinity index	Mesophase content
—	0.53	—
5	0.26	0.25
10	0.27	0.24
15	0.38	0.15
20	0.37	0.14
30	0.38	0.14

are not clear. It is believed that the length of the aliphatic tail of the stearic acid is too short to entangle and cocrystallize with the polypropylene molecules.³⁹ It is suggested that during polypropylene crystallization, liquid stearic acid deactivates the heterogeneities originally present in the polymer melt and blocks or destroys polypropylene nuclei.³¹ This results in reducing the crystallization rate.

Similarly, by formation of polypropylene/stearic acid fibers, the molecules of the acid hinder molecular motions necessary for polypropylene crystallization and retard the nucleation and/or growth of polypropylene crystals.

The influence of stearic acid on the polypropylene crystallization depends on acid concentration. For higher concentration, the effect of the stearic acid on the fibres structure is smaller. The fibers are more crystalline and their structure show up to be more similar to the structure of pure polypropylene fibers. In this case, cooling of polypropylene/stearic acid solution induces sharp separation of the components. Polypropylene crystallizes forming high crystalline structure and stearic acid hinders polypropyl-

ene crystallization to a lesser extent. Molecules of stearic acid are expelled from growing polypropylene crystals and form the separate phase.

For lower acid concentration, the effect of stearic acid on polypropylene crystallization is greater. With the decrease of the acid concentration, the mesophase content in fibres increases. It means, that stearic acid hinders polypropylene crystallization and interacts with polypropylene chains more intensively. During phase separation, stearic acid dimers disintegrate and long aliphatic tails of stearic acid molecules probably entangle partially at least in the amorphous regions of the fiber.

By further cooling in the temperature below 70°C, drops of liquid stearic acid solidify. With the purpose of removing solid stearic acid from the as-spun fibers, treatment in the KOH solution was performed. During such treatment, the saponification of stearic acid occurred. The potassium stearate, which is water-soluble, was formed. In this form stearic acid can be removed from the fibers by rinsing in water.

The transformation of the stearic acid into a potassium soap inside the fiber and its removal from fibers is documented by FTIR spectra (Fig. 5).

On the spectra for fibers after alkali treatment and rinsing close to 1500 cm⁻¹, two characteristic bands are visible. The bands come from asymmetric and symmetric stretches of two C—O bonds in the potassium stearate. For fibers extruded at the lowest stearic acid concentration bands exhibit the highest absorption. By increasing the stearic acid concentration, the intensity of the bands decreases.

The higher absorption of the band is connected with higher concentration of potassium stearate

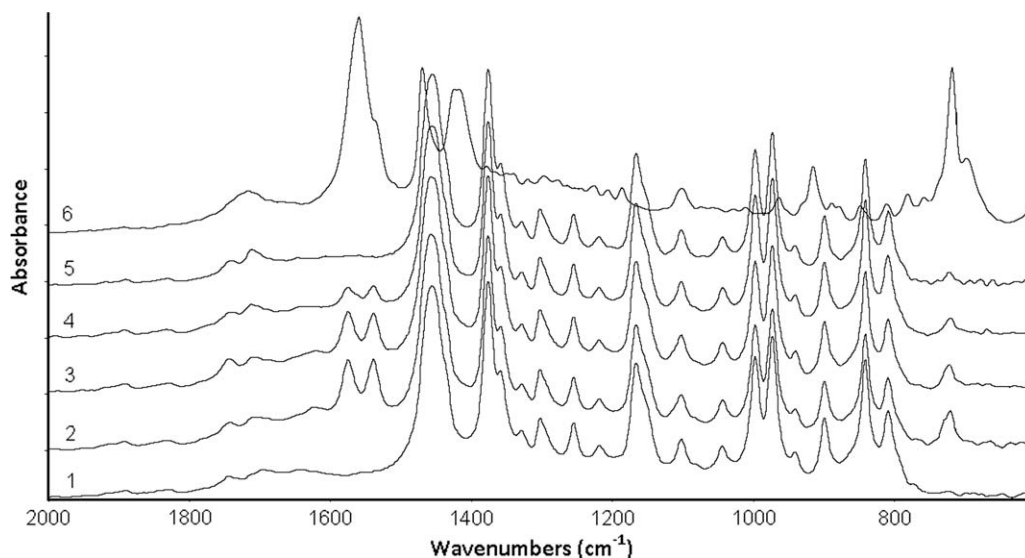


Figure 5 FTIR spectra for fibers after alkali treatment and rinsing: 1/pure polypropylene fibers; 2/polypropylene/stearic acid fiber (5% of stearic acid); 3/polypropylene/stearic acid fiber (10% of stearic acid); 4/polypropylene/stearic acid fiber (15% of stearic acid); 5/polypropylene/stearic acid fiber (30% of stearic acid); 6/calcium stearate.

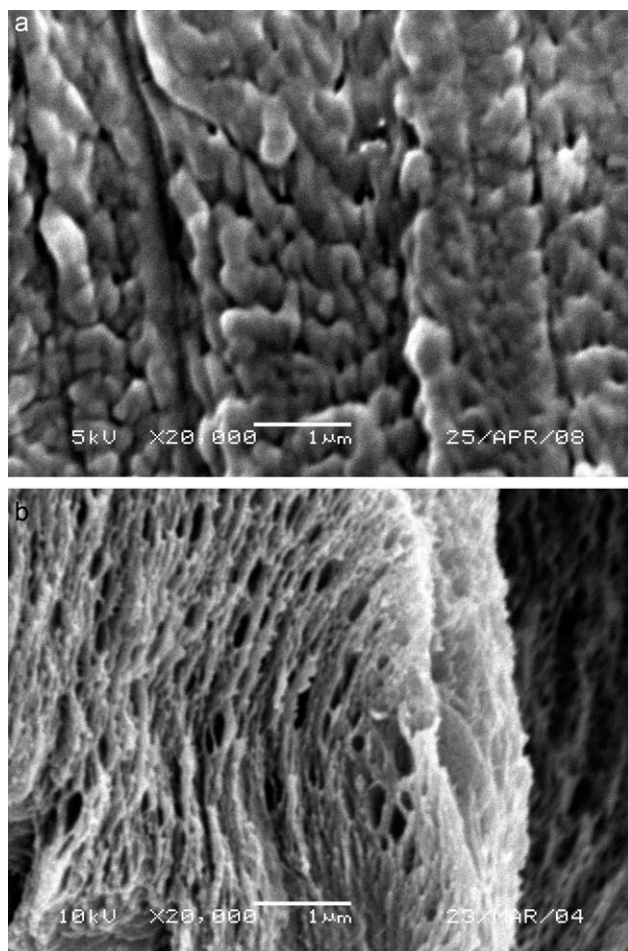


Figure 6 (a) and (b) The SEM microphotograph of the cross-section of the fibers after alkali treatment and rinsing (concentration of stearic acid 30%).

remaining inside fibers after alkali treatment and rinsing. According to previous statements by low acid concentration stearic acid is stronger connected to polypropylene matrix and its removing from the fibers is more difficult. By higher concentration, stearic acid forms separate phase and the extraction of the potassium stearate occurs much easier.

After alkali treatment and rinsing inside fibers, the porous system is produced. Figure 6 presents microphotographs of fibers extruded from the blend containing 30% of stearic acid. The porous structure occurs across the entire fiber cross-section. In the whole cross-section, independently of the distance from the fiber surface, pores possess the similar dimensions 0.1–0.5 μm .

CONCLUSIONS

The extrusion of polypropylene/stearic acid blend leads to the formation of fibers that contain drops of stearic acid trapped in polypropylene matrix. During solidification of the fibers, interaction between poly-

propylene and stearic acid is observed. Stearic acid slows down polypropylene crystallization and disturbs the formation of well ordered crystalline structure. As a result, the structure containing significant amount of mesophase is formed inside the fibers. The content of mesophase depends on stearic acid concentration. The highest mesophase content was observed for fibers extruded by low stearic acid concentration. In this case, partial incorporation of long aliphatic tails of the stearic acid into polypropylene structure was observed. For higher acid concentration, the mesophase content decreases. Fibers have more crystalline structure, which is more similar to the structure of pure polypropylene fibers.

Alkali treatment followed by water rinsing enables only partial removing of stearic acid drops from the fibers. After extraction of potassium stearate, the porous structure is formed inside fibers. Pores occur across the entire fiber cross-section.

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