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Structure of polypropylene fibres coloured with a mixture of pigments with different nucleating ability

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Abstract

Investigations of the structure of polypropylene fibres coloured with a mixture of quinacridone and phthalocyanine pigments were carried out. The structure of the fibres, evaluated by wide-angle X-ray scattering and small-angle X-ray scattering methods, was compared to the structure of noncoloured fibres and the fibres coloured with particular pigments. It was stated, that pigments participate in the nucleation process at low take-up velocity. In the presence of pigments, nuclei of two polymorphic forms α and β are formed. In fibres coloured with the mixture of pigments the competition between formation of the α and β nuclei occurs. The β nuclei formed on the crystals of the quinacridone pigment dominate. The high number of the β nuclei, together with the higher growth rate of the β crystals, leads to the formation of a structure containing a large amount of the β form, only slightly lower in comparison to the fibres coloured with the quinacridone pigment. At higher take-up velocities under higher molecular orientation in the cooled stream of the fibre, the very effective row nuclei are produced. In the presence of such nuclei, pigments do not participate in the nucleation process and do not affect the fibre structure.

Keywords: Polypropylene fibre; Structure; Pigment

1. Introduction

Polypropylene fibres cannot be dyed with dyestuffs and bath methods commonly applied to other fibres. Due to a nonpolar paraffinic character, their dyeing is performed during spinning in a mass colouration process [1].

For the mass colouration of the polypropylene fibres inorganic and organic pigments are applied. Among inorganic pigments titanium dioxide and carbon black, pigments commonly used for colouring to white and black colours, possess the greatest importance. To obtain colouristic effects usually the organic pigments with sufficient heat resistance are applied. In many cases the use of a mixture of two or more different pigments is required.

Pigments added to the polymer melt during extrusion participate in the crystallisation process leading to the formation of the fibres structure. The influence of pigments on the crystallisation process reflects in the fibres structure and subsequently in the fibres properties [2,3].

Several pigments reveal a good nucleating ability and accelerate the polypropylene crystallisation. Out of many pigments especially quinacridone and phthalocyanine possess high nucleating efficiency.

The quinacridone pigment as well as the phthalocyanine pigment occur in a crystalline state. Several polymorphic forms of pigment crystals provide differently shaped surfaces which can match the polypropylene chains. As a result of the interaction between the polypropylene molecules and the surface of the pigment crystals two polymorphic forms of polypropylene α and β can be obtained.

During crystallisation of the polypropylene melt with the addition of the mixture of the quinacridone and the phthalocyanine pigments the nuclei of both polymorphic forms of polypropylene are formed [4]. One can assume that there is a competition between the formation of both nuclei, which together with a different growth rate of the α and β crystals, leads to the formation of the structure containing a different content of both forms.

The nucleating efficiency of pigments, observed during crystallisation of the quiescent melt of polypropylene, is strongly limited by the fibres formation. During the fibres formation the orientation strongly influences the polypropylene crystallisation and the nucleating effect of pigments

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is visible only by appropriate selection of the formation parameters [5,6].

The aim of this work is the evaluation of the structure of fibres coloured with the mixture of quinacridone and phthalocyanine pigments extruded at different formation conditions. The structure of fibres will be analysed in comparison to the structure of fibres coloured with singular pigments as well as with the structure of noncoloured fibres.

2. Experimental

2.1. Samples

The investigations were carried out for noncoloured and coloured polypropylene fibres. The commercial isotactic polypropylene—Mosten 52.945 supplied by Chemopetrol (Czech Republic) and characterised by a melt flow index (MFI) of 25 g/10 min was used. The two pigments: quinacridone—Pigment Violet 19, C.I.73900 (Echtrot E3B—Hoechst, Germany) and phtalocyanine—Pigment Blue 15, C.I. 74160 B (Wola Kszysztoporska—Poland) were used to colour the fibres. The fibres coloured with singular pigments as well as with the mixture of pigments consisting of 50% of each pigment were produced.

Fibres were formed in laboratory conditions by means of a Brabender extruder. The polymer granulate was blended with the powdered pigments at the concentrations 0.5% by weight. Pigments were homogenised with the polypropylene melt in a barrel of the screw extruder. Barrel temperatures were 180, 190 and 200 °C, respectively, for the three barrel zones.

The melt was extruded through a five-hole spinneret die with a diameter of 0.2 mm. The extrusion temperature was maintained at 210 °C and the mass throughput was 3 g/min. The extruded filament was cooled in the air at 20 °C. The fibres were spun on to a winding roller with a take-up velocity varying from 100 to 1350 m/min.

The as-spun fibres with the linear density varying from 7 to 50 dtex were obtained.

2.2. Measuring methods

The investigations of the fibre structure were carried out by means of the wide-angle X-ray scattering (WAXS) and the small-angle X-ray scattering (SAXS) methods.

The WAXS investigations were performed with an X-ray diffractometer HZG-4 for the powdered samples obtained on a Hardy microtome. The diffraction patterns were registered in the angular range from 5 to 35°.

The WAXS pattern analysis was carried out by using Hindeleh–Johnson method [7] constructing a theoretical curve approximating the experimental curve. The theoretical curve was constructed as a sum of functions describing crystalline or mesophase peaks, an amorphous halo and a background scattering. Component functions parameters were calculated by minimisation of the sum of squared deviations of the theoretical curve from the experimental one. The minimisation was carried out according to Rosenbrock's method by means of a computer program OptiFit [8].

On the basis of the received patterns a mesophase content, a crystallinity index and the β form content were calculated. The crystallinity index and the mesophase content were calculated as a ratio of the area under crystalline or mesophase peaks to the total area. The content of the β form was determined using the equation of Turner-Jones [9]

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

where $I_{(300)_\beta}$, the height of the characteristic β form peak (300), whereas $I_{(110)_\alpha}$, $I_{(040)_\alpha}$ and $I_{(130)_\alpha}$ are heights of the strong α form peaks (110), (040) and (130), respectively.

The SAXS investigations were performed by means of a MBraun SWAXS camera utilising a conventional Kratky collimating system. The camera was mounted on the top of the tube shield of a stabilised Philips PW 1830 X-ray generator.

The scattered radiation was registered in the direction along the fibres axis for a bundle of parallel aligned fibres placed in a vacuum chamber. The measurements were carried out in the range from 0 to 5° with a position sensitive counter.

The experimental SAXS curves were desmeared using the direct method of the desmearing procedure implemented on MBraun software (3DV) [10].

On the basis of the SAXS investigations the long period and the lamellae thickness were calculated. The long period was estimated from the position of the peak using Bragg's law. The lamellae thickness was calculated by multiplication of the long period by the volume fraction of the ordered phases estimated by WAXS investigations.

3. Results

3.1. WAXS

Fig. 1 presents series of WAXS patterns obtained for noncoloured and coloured fibres extruded at different take-up velocities.

With fibres taken at the lowest take-up velocity 100 m/min on a pattern obtained for the noncoloured fibres crystalline peaks of the α form of polypropylene are visible (Fig. 1(a)). With the coloured fibres, besides the crystalline α peaks, the strong (300) peak characteristic for the β form of polypropylene appears. In the case of fibres coloured with the quinacridone pigment the (300) peak possesses a very high intensity. Conversely, for fibres containing the

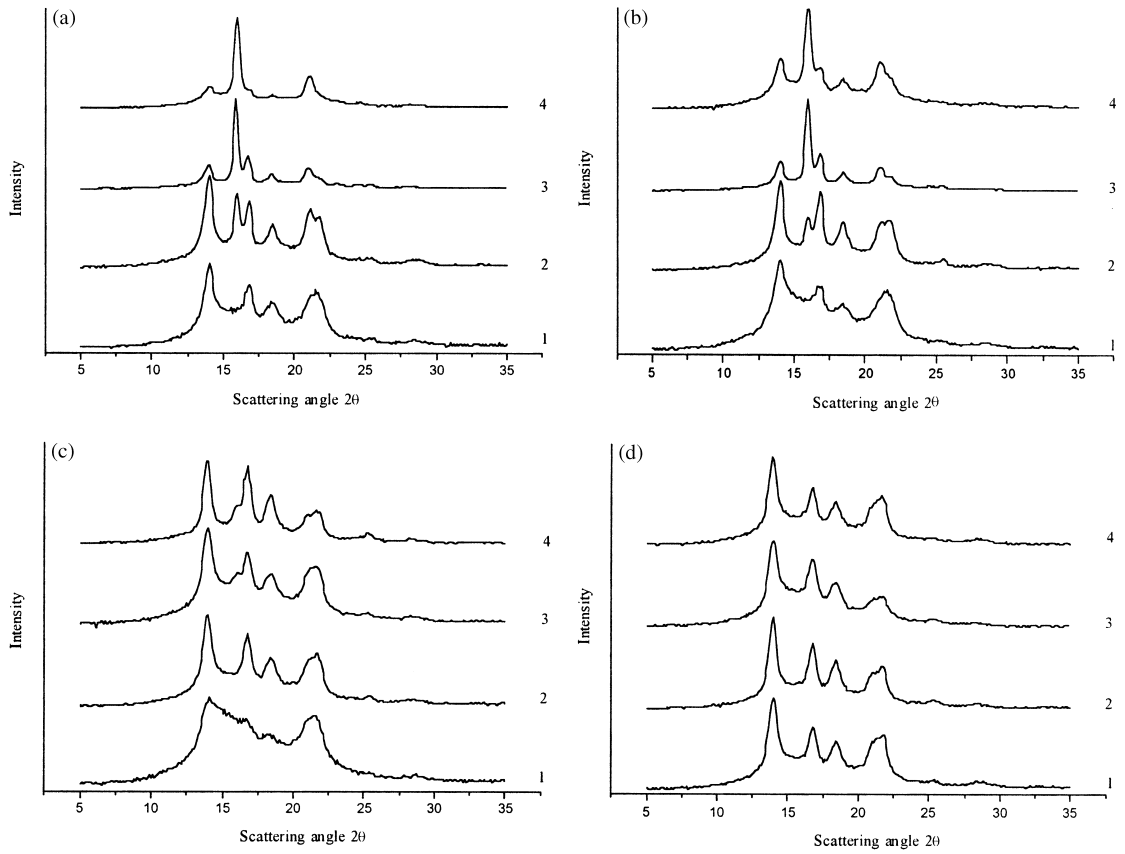

Fig. 1. WAXS patterns of the polypropylene fibres taken at: (a) 100 m/min, (b) 200 m/min, (c) 400 m/min, (d) 1350 m/min ((1) noncoloured fibres, (2) fibres coloured with the phthalocyanine pigment, (3) fibres coloured with the mixture of pigments, (4) fibres coloured with the quinacridone pigment).

phthalocyanine pigment the intensity of the (300) peak is much lower and it is comparable with intensities of the α form peaks. With fibres coloured with the mixture of pigments the intensity of the (300) peak is only slightly lower in comparison to the fibres coloured with the quinacridone pigment.

On patterns obtained for fibres taken at the slightly higher take-up velocity 200 m/min the crystalline peaks observed for the noncoloured fibres overlap two broader mesophase peaks (Fig. 1(b)). In the case of the coloured fibres, the intensity of the characteristic (300) peak decreases, whereas the intensity of the α peaks increases.

The intensity of the mesophase peaks in the noncoloured fibres increases together with further increment of the take-up velocity, while the intensity of the (300) peak of the β form in the coloured fibres decreases. For fibres taken at the 400 m/min the mesophase peaks in the noncoloured fibres become so strong that the good resolved crystalline peaks are slightly visible (Fig. 1(c)). In the case of coloured fibres the (300) peak is visible only in fibres coloured with the quinacridone pigment and with the mixture of pigments. For fibres coloured with the phthalocyanine pigment the pattern reveals only α crystalline peaks.

The mesophase peaks become weaker at higher velocities as a result of the increase of the take-up velocity. At the highest take-up velocity 1350 m/min both the mesophase peaks and the (300) peak are not more observed in the coloured fibres. The WAXS patterns for all fibres independent of the presence of pigments contain only peaks characteristic for the α form of polypropylene (Fig. 1(d)).

During formation of the polypropylene fibres three phase structure, consisting of amorphous phase, mesophase and crystalline phase, is formed. The changes in the peak intensities observed on the WAXS patterns result from the change in the amount of the particular phases in the fibres structure. The parameters, which characterise the content of the phases calculated according to the WAXS patterns are presented in Table 1.

3.2. SAXS

With all investigated fibres SAXS patterns exhibit a distinct maximum of a long period, whose intensity and angular position changes with the increase in the take-up velocity and the addition of pigments. Fig. 2 shows an example of the SAXS curve obtained for fibres coloured with the quinacridone pigment taken at 880 m/min.

In the case of fibres taken at the lowest take-up velocity the maximum occurs at the lowest angle. With fibres taken at velocities from 100 to 400 m/min the peak moves to the higher angles. Further increase in the take-up velocity

Table 1
The phase content in polypropylene fibres taken at different take-up velocity

	Take-up velocity (m/min)	Crystallinity index	Mesophase content	*K*-value
Noncoloured fibres	100	0.42	–	–
	200	0.40	0.10	–
	300	0.34	0.16	–
	400	0.32	0.19	–
	880	0.33	0.17	–
	1050	0.35	0.16	–
	1350	0.53	–	–
Fibres coloured with the phthalocyanine pigment	100	0.53	–	0.16
	200	0.53	–	0.09
	300	0.53	–	–
	400	0.51	–	–
	880	0.52	–	–
	1050	0.52	–	–
	1350	0.52	–	–
Fibres coloured with the mixture of pigments	100	0.53	–	0.75
	200	0.52	–	0.52
	300	0.53	–	0.14
	400	0.51	–	0.05
	880	0.52	–	0.04
	1050	0.51	–	–
	1350	0.52	–	–
Fibres coloured with the quinacridone pigment	100	0.55	–	0.80
	200	0.52	–	0.58
	300	0.51	–	0.18
	400	0.51	–	0.06
	880	0.51	–	0.06
	1050	0.51	–	0.07
	1350	0.52	–	–

causes the shift in the peak position back toward the lower values.

The shift in the peak position observed with the change in the take-up velocity reflects the change in the long period.

Fig. 3 shows the values of the lamellar thickness calculated for noncoloured and coloured fibres taken at different velocities.

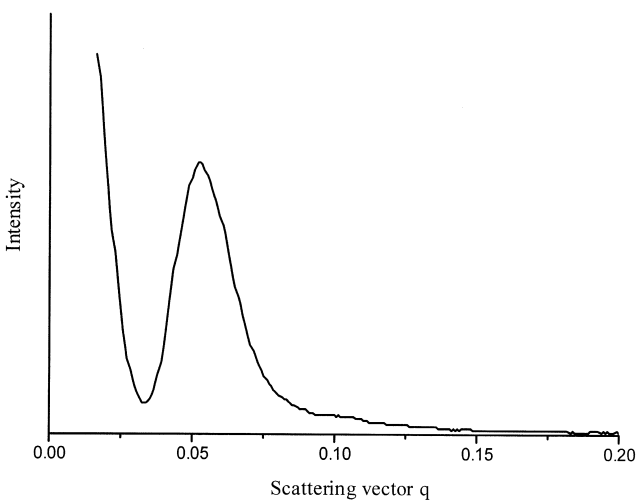

Fig. 2. SAXS curve of the fibres coloured with the quinacridone pigment taken at 880 m/min.

4. Discussion

The fibres structure is formed as a result of the crystallisation process, which occurs during solidification of the extruded stream of the fibres. For noncoloured fibres

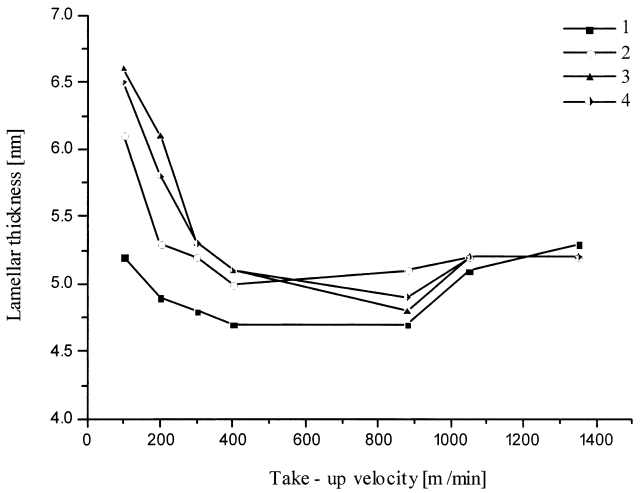

Fig. 3. The lamellar thickness of the polypropylene fibres: (1) noncoloured fibres, (2) fibres coloured with the phthalocyanine pigment, (3) fibres coloured with the mixture of pigments, (4) fibres coloured with the quinacridone pigment.

the course of the crystallisation process depends on the cooling rate and molecular orientation, which are affected by the formation parameters. In the case of coloured fibres, apart from the parameters mentioned above, the crystallisation process is influenced by the presence of pigments.

In fibres taken at low take-up velocities the molecular orientation is minimal and does not influence the polypropylene crystallisation. In such conditions, the crystallisation process proceeds similarly as in a nonoriented system. The rate of the crystallisation depends on the cooling rate of the extruded stream and in the case of coloured fibres additionally on the presence of pigments.

At lowest take-up velocity of 100 m/min the cooling rate achieves the lowest value. Then the crystallisation process proceeds at the highest temperature producing lamellae with the highest thickness. In such conditions the crystalline structure consisting of the α form is formed in noncoloured fibres. In coloured fibres apart from the α form, the crystals of the β form appear as well. The highest β form content is observed when fibres are coloured with the quinacridone pigment (Fig. 4). With fibres coloured with the phthalocyanine pigment the amount of the β crystals is repeatedly lower. In the case of fibres coloured with the mixture of pigments the β form content scarcely changes in comparison to fibres coloured with the quinacridone pigment.

The α and β forms of polypropylene are produced in similar preparation conditions and their formation depends mainly on nucleation process [11].

Pigments in fibres taken at the lowest take-up velocity participate in the nucleation process. As a result of the nucleating effect of pigments the crystallisation temperature in coloured fibres increases in comparison to the noncoloured fibres. The higher crystallisation temperature reflects in the higher lamellar thickness.

The crystallisation temperature in coloured fibres

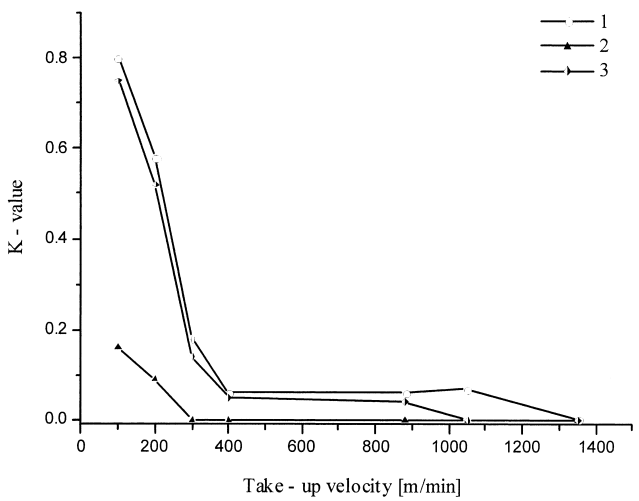

Fig. 4. The β form content in the coloured fibres taken at different velocities. (1) fibres coloured with the quinacridone pigment, (2) fibres coloured with the phthalocyanine pigment, (3) fibres coloured with the mixture of pigments.

achieves the value above the lower critical temperature T^{**}_c for the formation of the β form of polypropylene [12].

In this temperature a great number of the β nuclei is formed on the surface of the quinacridone crystals.

The nucleating ability of quinacridone pigment to produce the β form of polypropylene is well known [13,14]. On the *bc* surface of quinacridone γ form crystals the aromatic rings of linear stacked molecules form a parallel array of bulges and ditches. The spacing between ditches equals to 0.67 nm and is close to the polypropylene helix axis distance 0.65 nm. The conformity of those dimensions ensures nearly perfect match of polypropylene chains with the surface of the quinacridone crystals. Absorption of polypropylene chains perpendicularly to the parallel ditches enables the epitaxial growth of the β form of polypropylene [15,16].

In temperature above T^{**}_c the growth rate of the β form crystals exceeds the growth rate of the α crystals [17]. The β form nuclei formed on the surface of the quinacridone crystals quickly grows forming the high amount of the β form crystals.

During crystallisation the temperature successively decreases and moves into the range below the T^{**}_c. Then the remaining crystallizable material crystallises further at lower temperature producing small amount of the α form crystals.

In the case of fibres coloured with phthalocyanine pigment the appearance of the small amount of the β crystals seems to be surprising. The phthalocyanine pigment is known as an efficient nucleant of the α form of polypropylene [18]. The formation of the β form by addition of this pigment has not been observed so far.

In the phthalocyanine crystals the stacked molecules expose aromatic rings which form shallow ditches on the crystal surface. The polypropylene chains absorbed in such ditches are forced to assume a stretched conformation. In this way the free energy of formation a critical nucleus decreases. The nucleation mechanism described above served so far as the explanation of the α nuclei formation. However, when analysing the surface geometry of the α form of the phthalocyanine crystal, one may notice that the spacing between ditches equals to 1.19 nm [19]. This value is close to the spacing of 1.1 nm between helices of the same hand in the β form of polypropylene [20].

The compatibility of those dimensions enables the formation of the β nuclei [21] and may be an explanation of the formation of the certain number of the β nuclei in fibres coloured with the phthalocyanine pigment.

Taking into account the higher growth rate of the β crystals one can suppose that the fraction of the β form in fibres is higher than the fraction of the β nuclei.

Respecting previous statements as well as the low β form content it can be concluded that in fibres coloured with phthalocyanine pigment only a few β nuclei are formed. The addition of this pigment first and foremost causes the formation of the α nuclei of polypropylene.

In fibres coloured with the mixture of pigments both pigments may participate in the nucleation process. Taking into account the similar degree of the fineness of pigment crystals one can assume that inside the crystallising stream the number of the quinacridone crystals producing the β nuclei in good approximation equals to the number of the phthalocyanine crystals producing the α nuclei. Both pigments reveal their nucleating activity at similar temperature and the formation of the α and the β nuclei is expected. Surely, during the nucleation process a competition between nuclei formation occurs.

The high content of the β form obtained in the fibres coloured with the mixture of pigments is only slightly lower in comparison to the fibres coloured with the quinacridone pigment and points out that the formation of the β nuclei on the quinacridone pigment dominates.

The amount of the β crystals is not in direct proportion to the number of produced nuclei. Surely, the fraction of the β nuclei is not so high as the fraction of the β form in the coloured fibres.

As mentioned before, the growth rate of the β form in the temperature above the critical temperature T^{**}_c is higher than the growth rate of the α form. During crystallisation the faster growing β crystals constrain the growth of the α crystals. As a result, despite of the significant number of the α nuclei, their effect on the fibres structure is less visible and the structure characterised by the very high content of the β form is formed.

Conditions for the crystallisation process change for fibres taken at higher velocities. The increment in the take-up velocity results in the increase of the cooling rate and the increase of the molecular orientation. In the range of lower take-up velocity up to 400 m/min the effect of the molecular orientation is low. The cooling rate dominates the crystallisation process [22].

The higher cooling rate shifts the crystallisation temperature to the lower values. In consequence the lamellar thickness in all fibres decreases.

As a result of the higher cooling rate at take up velocity 200 m/min in noncoloured fibres the mesophase appears. With the increment in the take-up velocity to 400 m/min the mesophase content increases. The increment in the mesophase content is connected with the decrease in the amount of the crystalline phase.

With coloured fibres the increase in the take-up velocity does not cause any changes in the content of the crystalline phase. The crystallinity index in fibres, independent of the take-up velocity, achieves the same value. The increment in the take-up velocity produces the significant change within the crystalline phase, inducing a drastic change in the portion of the individual polymorphic forms.

The observed changes result from the change in the crystallisation conditions. The shift in the crystallisation temperature toward lower values brings it closer to the critical temperature T^{**}_c. Then the crystallisation starts at the temperature above T^{**}_c and then moves quickly below this temperature. In consequence the smaller part of the material crystallises in conditions favourable for the formation of the β form, hence the β form content in fibres decreases.

In fibres coloured with the quinacridone pigment taken at 200 m/min, the β form content decreases only slightly. With further increment in the take-up velocity the β form content drastically drops, so in fibres taken at 400 m/min the β form is hardly visible.

In the case of fibres coloured with phthalocyanine pigment small amount of the β form occurs in fibres taken at the 200 m/min. Then for higher velocities the structure contains only the α crystals.

With fibres coloured with the mixture of pigments similarly as for fibres coloured with the quinacridone pigment the β form content slowly decreases. However, the β form maintains in fibres with the increment in the take- up velocity of up to 400 m/min.

With the increase in the take-up velocity the molecular orientation grows and its influence on the crystallisation process increases. Under the orientation certain segments of polypropylene chains straighten up. The bundles of aligned chains form row nuclei, which act as very efficient nuclei for the polypropylene crystallisation. The crystallisation on the row nuclei proceeds very quickly and leads to formation of the α crystals.

The first row nuclei appear inside the cooled stream at the medium take-up velocity of 400 and 880 m/min. As a result the drop in the crystallisation temperature is stopped, despite the fact that the cooling rate continuously increases. The crystallisation temperature passes through the minimum and then slowly increases with the further increase in the take-up velocity.

At medium velocities, as a consequence of the low crystallisation temperature, the lamellae with the lowest thickness are produced.

The formation of the row nuclei causes the decrease in the mesophase content in the noncoloured fibres. In the case of the coloured fibres the row nuclei are formed together with the heterogeneous nuclei. In such conditions, at relatively low temperature, both nuclei produce the α form crystals and their contribution into the nucleation process is difficult to determine.

With the increment in the take-up velocity the number of the row nuclei increases, so at the highest velocities the large number of the row nuclei is produced. As a result, in noncoloured fibres the mesophase disappears and only the crystalline phase containing α form crystals is produced.

In coloured fibres taken at the highest velocities the crystallisation occurs first and foremost with the participation of the row nuclei, so the nucleation process on the pigment crystals loses its importance. At the highest take-up velocity 1350 m/min the pigments do not participate in the nucleation process.

The crystallisation in fibres coloured with particular pigments as well as with the mixture of pigments occurs at

the conditions similar to the noncoloured fibres. The process proceeds according to the same mechanism based on the formation of the row nuclei. As a result, in all fibres the structure consisting of the α modification characterised by the same crystallinity index and the same lamellar thickness is produced.

5. Conclusions

Pigments influence the fibres structure in the case of fibres taken at the low velocities. With the increase in the take-up velocity the effect of pigments on the fibres structure is weaker, so at the highest velocities their influence becomes not visible.

At the lowest take-up velocity pigments characterised by the high nucleating efficiency participate in the nucleation process. At medium velocities, under the higher molecular orientation inside the cooled stream, the row nuclei are formed. With the increase in the take-up velocity, the number of the row nuclei increases, so in fibres taken at the highest velocity a great number of them is produced. In the presence of very active row nuclei the heterogeneous nuclei formed on pigments crystals become insignificant. In fibres taken at the highest velocity, the crystallisation process occurs only on row nuclei which are formed without pigments.

In fibres taken at low take-up velocity, in the presence of the quinacridone pigment, the structure with the high content of the β form is produced. In fibres containing the phthalocyanine pigment the structure formed mostly from the crystalline α form is observed. In the case of fibres coloured with the mixture of pigments, the competition between α and β nuclei occurs. The β nuclei formed on the quinacridone pigment dominate and the structure with the high β form content is formed. The high amount of the β crystals, which occurs in the fibres coloured with the mixture of pigments, is only minimally lower in comparison to the fibres coloured with the quinacridone pigment. It results not only from the domination of the β nuclei, but also from the higher growth rate of the β crystals.

With the increase in the take-up velocity the β form content in coloured fibres gradually decreases, so at higher velocities the β form disappears. The decrease in the β form content results initially from the change in the crystallisation temperature and then for higher velocities from the formation of the very efficient row nuclei.

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