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Structure of Polypropylene Fibres Coloured with Organic Pigments

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1. Introduction

Polypropylene is known as a versatile and valuable fibre-forming polymer material, which is widely used for the production of medical and hygienic products, carpets and floor coverings, apparel and household textiles, filtering media, agro and geotextiles, automotive interior and many other technical textiles. The wide range of goods comprises a variety of products including mono- and multifilaments, staple fibres, tapes and fibrillated fibres as well as spun-bonded and melt-blown nonwovens.

For the formation of polypropylene textiles different techniques were developed. The common method used for the formation of mono- and multifilaments is classical melt spinning.

In melt spinning, polypropylene in powder or pellet form is heated above the melting point and then is extruded through fine orifices of a spinneret into the air. Below spinneret in the air thin streams are intensively cooled and subjected to an intense stretching. During cooling the liquid streams solidify. Finally, solidified filaments are taken by final take-up device.

Formation of fibres with good properties requires proper selection of formation parameters. Changes of the particular parameters have a great impact on the fibres' structure.

The significant changes of the fibres' structure were observed right from the beginning of their production (Natta, 1961; Ross, 1965; Sheehan & Cole, 1964). It was stated that inside the fibres both, less ordered mesophase and well ordered crystalline phase can be formed.

Mesophase reveals intermediate order between amorphous and crystalline phases. In the first studies it was labelled as smectic (Natta & Corradini, 1960) or paracrystalline (Miller, 1960). Further studies revealed that mesophase is made up of bundles of parallel chains, which maintain typical for all polymorphic forms of polypropylene three-fold helical conformation. Bundles are terminated in the direction of the chain axis by helix reversals or other conformational defects (Androsch et al., 2010). In the bundles long range ordering maintains only along the chain axes, whereas in lateral packing a large amount of disorder is present (Natta & Corradini, 1960). The mesophase is formed by quenching of the molten polypropylene (Miller, 1960; Wyckoff, 1962) or by deformation of the crystalline structure (Saraf & Porter, 1988; Qiu, 2007). As for the fibres, the mesophase was observed in fibres taken at low take-up velocity (Spruiell & White, 1975; Jinan et al., 1989, Bond & Spruiell, 2001) in fibres intensively cooled in water with addition of ice or in the mixture of dry ice

and acetone (Sheehan & Cole, 1964; Choi & White, 1998; Yu & White, 1999; Choi & White, 2000), in fibres extruded at the high extrusion temperature (Dees & Spruiell, 1974) and fibres extruded from polypropylene with low molecular weight (Lu & Spruiell, 1987).

The content of the mesophase significantly decreases in fibres taken at other parameters. At certain conditions the mesophase completely disappears and inside fibres only two-phase structure, crystalline and amorphous, is formed. The high crystalline content was obtained in fibres extruded at low extrusion temperature and taken at high take-up velocities (Spruiell & White, 1975; Bond & Spruiell, 2001).

Investigations of the crystalline structure revealed that inside the fibres the crystalline phase is usually built from α crystals. The α form is one of the three known polymorphic forms of polypropylene (Brückner et al.,1991; Lotz et al., 1996). It can be easily obtained by crystallization of polymer melts or solutions. It is the most stable and the most often encountered form in different polypropylene products.

The structure of the α form was early established. Natta and Corradini (Natta & Corradini, 1960) proposed a model based on the monoclinic unit cell. According to this model, polypropylene helices of the same hand are arranged in layers parallel to the *ac* plane. Layers of isochiral helices alternate with layers formed from helices of the opposite hand. The model was commonly accepted and confirmed by subsequent studies of Mencik (Mencik, 1972), Hikosaka (Hikosaka & Seto, 1973) and Corradini (Corradini et al., 1980).

During investigations of the fibres' structure in few cases, except commonly encountered α form, crystals of β form were observed. The β form occurs rarely in the polypropylene products and its formation requires special crystallization conditions. It was revealed that the β form arises during crystallization of a sheared melt (Leugering & Kirsch, 1973), crystallization in a temperature gradient (Lovinger et al., 1977) or during crystallization in the presence of special additives (Tjong et al., 1996; Varga, J. et al. 1999; Li & Cheung, 1999; Varga, 2002). The β form was obtained in the case of fibres containing efficient β nucleating agents and extruded at appropriately selected spinning parameters (Yu & White, 2001; Takahashi, 2002).

The β form exhibits complex structure and during the years different models characterizing this structure were proposed. Finally, the arrangement of the β form was discovered only several decades after its initial observation. It was shown that the β form consists of the characteristic left-handed or right-handed helices arranged in the original packing schemes. Lotz (Lotz at al, 1994) and Meille (Meille at al., 1994) proposed a model of the frustrated structure based on a trigonal cell containing three isochiral helices.

The structure of fibres is formed during the crystallisation, which occurs below spinneret orifices, in the cooling zone, by solidification of the extruded stream. The crystallization rate is comparable to the cooling rate of the polypropylene in the spinning line. Therefore, the formation of crystalline structure in the melt-spinning process depends strongly on the spinning conditions and polymer characteristics.

During the formation of fibres the crystallization takes place in non-isothermal conditions in the field of high tensile stress. Cooling rate and tensile stress strongly affect polypropylene crystallization.

During formation at low take-up velocities the cooling rate plays the dominant role. At low take-up velocity the cooling rate and the applied tensile stress are low. The crystallization proceeds at relatively high temperatures and in the as-spun fibres monoclinic α crystals are formed. When take-up velocity is increased the cooling rate is enhanced. Simultaneously, the crystallization temperature decreases. By crystallization in such conditions the structure with high mesophase content is formed. Further increase of take-up velocity leads to an increase of the tensile stress. Consequently, the molecular orientation of polypropylene chains increases significantly. At higher molecular orientation the crystallisation temperature increases. The crystallisation rate rapidly increases and the crystal structure with highly oriented monoclinic crystals is formed.

2. Dyeing of polypropylene fibres

Polypropylene fibres are highly crystalline and show extremely low wettability. Due to the aliphatic structure of the polypropylene chain fibres have no polar groups and no dye sites capable of reacting permanently with dye molecules. Therefore, polypropylene fibres cannot be coloured by bath methods commonly used for the coloration of other natural and synthetic fibres. Over the years many efforts were undertaken for improving the fibres' dyeability. Various methods include copolymerizing with other monomers, grafting of dye sites, adding dyeable polymers before fibres spinning, adding dyeable filaments before fibre processing, dissolving or dispersing additives of low molecular weight in the polymer melt, treating to modify the surface of fibres after extrusion or adding halogen compounds (Zhu & Yang, 2007). All mentioned techniques have not found broader commercial application. The mainstream technique for the coloration polypropylene fibres consists of using pigments. Despite of its disadvantages, low flexibility and suitability only for a large-scale manufacturing coloration with pigments has a great importance. The most coloured polypropylene textiles are made from fibres coloured this way.

Pigments used for the fibres coloration must be finely dispersed and stable to the thermal conditions and environment applied in fibres formation. Most of the pigments reveal tendency to agglomerate and form large aggregates, which clog the spinneret orifices and spoil the fibres properties. To avoid spinning problems, fine dispersed pigment concentrates, so called masterbatches, are commonly used. Pigment concentrates are made from previously dispersed pigments mixed with polypropylene resin at high pigment concentration. The concentrates are usually mixed in a proper ratio with polymer granulate or powder. Some concentrates are injected directly into the polypropylene melt during fibre formation.

For the coloration of polypropylene fibres inorganic and organic pigments are used. Most inorganic pigments reveal low to moderate colour strength combined with good to excellent thermal stability, lightfastness and weather resistance. Inorganic pigments are easily dispersible. For polypropylene coloration inorganic pigments for black and white colours are mostly applied. For this purpose carbon black and titanium dioxide white pigment based on the rutile modification are used.

Coloration effects are usually achieved with organic pigments. Organic pigments provide high colour strength and high light stability. Some pigments heave negative influence on the efficiency of light stabilizers and limited heat resistance. By reason of above mentioned negative influence only selected groups of pigments can be used. In the literature the

following groups of pigments are usually mentioned: azo pigments, isoidolinones, perylene, anthraquinone, quinacridone and phthalocyanine.

During mass coloration pigments are mixed physically with the polypropylene melt in the barrel of the extruder.

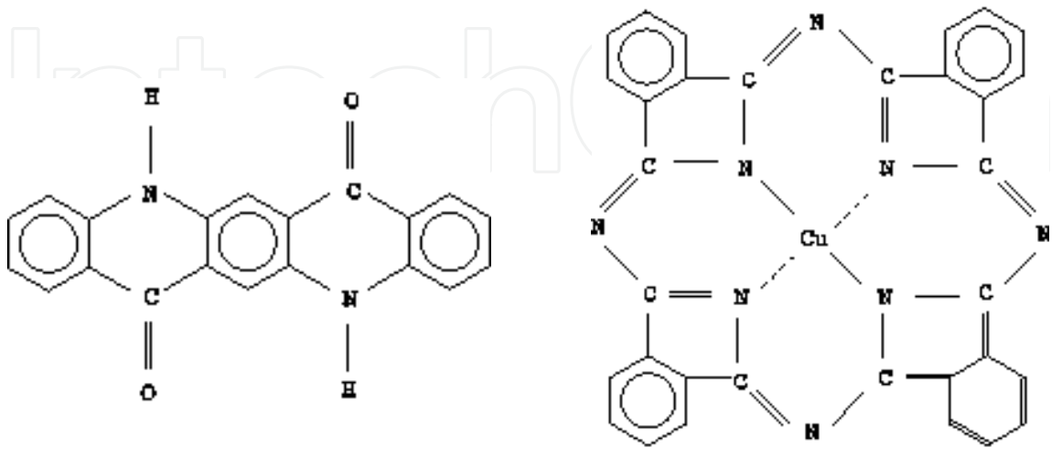
It is well known that impurities and foreign substances present in crystallizing polymer strongly affect its crystallisation. Impurities provide a foreign surface, what reduces free energy of the formation of primary nuclei and significantly reduces their critical dimensions. As a result of the formation of heterogeneous nuclei the nucleation density in the crystallizing melt significantly increases. Consequently, the crystallisation temperature is higher and the crystallisation rate rapidly increases.

On the basis of investigations of nucleating ability of many compounds Binsbergen revealed that good nucleating agents are insoluble in the polypropylene melt or crystallize earlier at higher temperature prior polypropylene crystallisation (Binsbergen, 1970). Pigments have such desired properties and fulfil requirements for good nucleating agents of polypropylene. The most pigments form stable crystals, which are insoluble in the polypropylene melt. The rough surface of pigments crystals enables the epitaxial growth of polypropylene crystals. The various geometries of the contact surface can lead to the formation of the different polypropylene modifications.

3. Nucleating ability of phthalocyanine and quinacridone pigments

The nucleating ability toward polypropylene crystallisation for some pigments was investigated and the efficient ability of quinacridone and phthlacyanine was revealed (Broda, 2003a). The investigation were performed in non-isothermal conditions by polarizing microscopy and differential scanning calorimetry (DSC).

Phthalocyanine and quinacridone belong to organic pigments, which are commonly used for the coloration of polypropylene fibres. The chemical formulae of pigments are presented in Figure 1.



a) b)

Fig. 1. Chemical formulae of: a) quinacridone, b)phthalocyanine blue

The blue phthalocyanine pigment (Pigment Blue 15, C.I.74160) is built of a tetrabenzoporphyrazine nucleus with a central copper atom. The molecule assumes a planar conformation and possesses a square shape with a side length of 1.3 nm. The red quinacridone pigment (Pigment Violet 19, C.I.73900) belongs to deeply colored pigments characterized by a relatively small molecular size. The molecule of dimensions 1.406 x 0.52 nm is formed from five heterocyclic rings. The molecule is planar with no significant departure of the carbonyl groups from a molecular plane defined by all nonhydrogen atoms.

Both pigments added to quiescent melt accelerate polypropylene crystallization. In the presence of pigments the crystallization temperature moves toward higher temperature. The increase of the crystallization temperature for phthalocyanine and quinacridone pigment is 13 K and 14.5 K, respectively (Broda et al., 2007). Such increase of the crystallization temperature is very high and comparable with the increase observed for effective nucleating agents. In the presence of pigments the nucleation density significantly increases. Consequently, the overall crystallization rate is enhanced and, as a result, fine spherulitic structure is formed.

The nucleating ability of both pigments results from their crystalline structure. Both pigments form fine dispersed crystals, which have very high thermal stability. The degradation temperature of phthalocyanine and quinacridone pigments is higher then 400 and 500 °C, respectively, what considerably exceeds the melting temperature of polypropylene.

The surface structure of pigments crystals enables the epitaxial growth of the polypropylene.

In crystals of the quinacridone pigment planar molecules are arranged in parallel stacks, with the molecule tilted to the stacking direction. The neighboring stacks adopt a herringbone arrangement. In crystals each molecule is bonded through hydrogen bonds to four adjacent molecules. Very strong intermolecular hydrogen bonds combined with strong van der Waals' forces ensure quinacridone pigments the high heat and chemical resistance.

Seven different crystalline forms of quinacridone are known (Filho & Oliveira 1992; Potts et al. 1994, Lincke, 2000). Most synthetic methods lead to the formation of an unstable α form. Subsequent treatments lead to the more stable β and γ forms, most commonly used as commercial pigments.

In the investigations the γ form of the quinacridone pigment was used. For years this modification has been known as a very efficient nucleating agent for the β form of polypropylene (Leugering, 1967; Moos & Tilger, 1981). Stocker and co-workers showed that the *β* form of polypropylene grows epitaxially on the surface of the γ crystals of the quinacridone pigment (Stocker et al., 1998). The epitaxy involves the (110) plane of the trigonal unit cell of the polypropylene, which contacts the *bc* surface of the γ crystals of the quinacridone.

Hydrogen atoms of stacked benzene rings form on the surface *bc* of the γ quinacridone crystals a parallel array of bulges and grooves. The spacing between grooves 0.65 nm is close to the axis repeat distance of the polypropylene helix. The arrangement of polypropylene chains on the pigment surface perpendicularly to the parallel grooves ensures nearly perfect matching of the above-mentioned dimensions and in this way enables the epitaxial growth of β crystals.

The formation of the β form is confirmed by WAXS measurements. In the WAXS pattern of polypropylene crystallized by addition of the quinacridone pigment characteristic β peaks are observed (Fig.2).

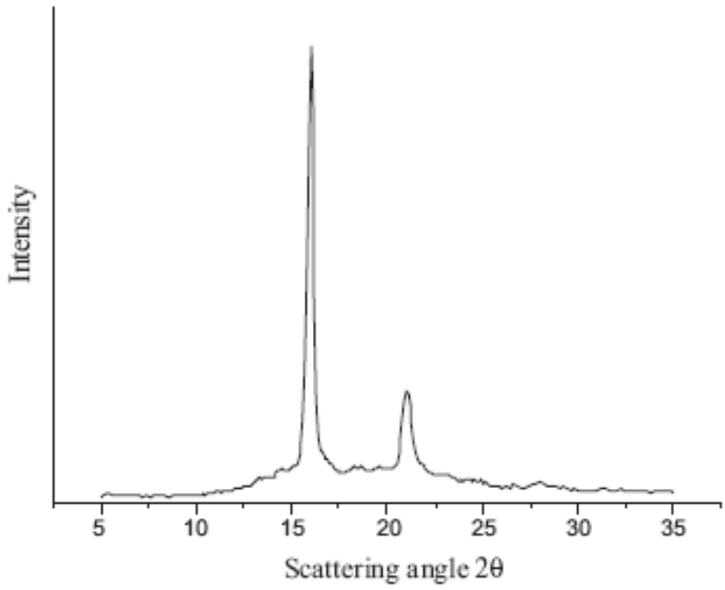


Fig. 2. WAXS pattern of polypropylene crystallized in the presence quinacridone pigment.

In crystals of the copper phthalocyanine fairly rigid molecules can be packed in different arrangements giving rise to different polymorphs. In literature ten different polymorphic forms of copper phthalocyanine are described (Erk & Hengelsberg, 2003). From all polymorphic forms commercial interest exhibits the first recognized α form and the most thermodynamically stable β form.

Each polymorphic form of phthalocyanine is built from molecules arranged in uniform stacks with rings tilted with respect to the stacking direction. For the α and β forms the molecules are tilted in stacks with respect to the stacking direction by 25° and 46°, respectively.

The interactions between molecules within stacks are mainly defined by π-π interactions. The interplanar distance between adjacent molecules is consistent with a van der Waals bond and equals 0.34 nm. In the β modification neighboring stacks are arranged in a herringbone style. In the α form the herringbone interactions are not present.

Crystals of phthalocyanine tend to form needles or rods parallel to the stacking direction. The side faces of crystals are mainly covered by aromatic hydrogen atoms, while the basal faces expose the π system and the copper atom. The lateral surfaces exhibit nonpolar character, while the basal surfaces have relatively polar character.

The aromatic hydrogen atoms occurring on the lateral surfaces of the pigments crystals are arranged in parallel rows. The shallow nonpolar grooves formed between such rows force polypropylene molecules to assume a stretched conformation over some distance, making the nucleation much easier (Binsbergen, 1970).

The investigated α form of phthalocyanine promotes mostly formation of the α form of polypropylene. On the wide-angle X-ray scattering (WAXS) pattern for polypropylene crystallized in the presence of phthalcoyanine pigment, crystalline peaks characteristic for the α form are observed (Fig.3).

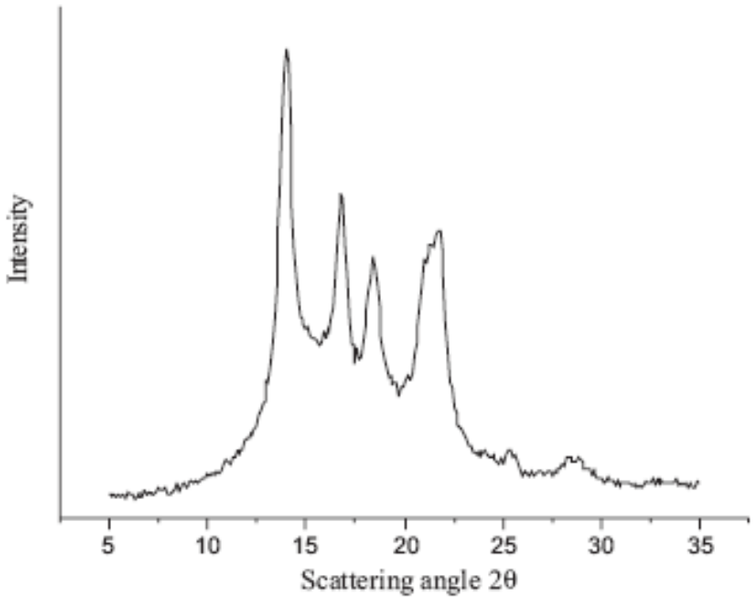


Fig. 3. WAXS pattern of polypropylene crystallized in the presence phthalocyanine pigment.

4. Structure of coloured fibres

The investigations of morphology and structure of coloured fibres were carried out. The morphology of fibres was investigated for samples sputtered with gold by scanning electron microscopy (SEM). The fibres structure was studied by the wide angle X-ray scattering (WAXS) and small angle X-ray scattering (SAXS) methods.

During formation of fibres coloured with pigments the structure containing crystalline, mesophase and amorphous phases is formed. Content of particular phases changes across a broad range depending on formation parameters.

4.1 Structure of fibres coloured with quinacridone pigment

Table 1 presents structural parameters determined on the basis of WAXS patterns for fibres coloured with quinacridone pigment.

For fibres taken at very low velocity 100 m/min the high crystalline structure without mesophase is formed. The structure consists mainly from β crystals with admixture of a small amount of α crystals.

The content of β form is usually characterised by the K value, which is determined as a ratio of the intensity of the $(300)_\beta$ peak to the sum of intensities of the $(110)_\alpha$, $(040)_\alpha$, $(130)_\alpha$ and $(300)_\beta$ peaks on the WAXS patterns (Turner Jones, 1964).

Extrusion temperature [°C]	Take-up velocity [m/min]	Crystallinity index	K value
210	100	0.54	0.95
	200	0.52	0.47
	300	0.51	0.09
	400	0.51	0.03
	880	0.51	0.03
	1050	0.52	0.03
	1350	0.52	-
250	100	0.51	0.93
	200	0.51	0.33
	300	0.50	0.08
	400	0.51	-
	880	0.52	-
	1050	0.52	-
	1350	0.52	-

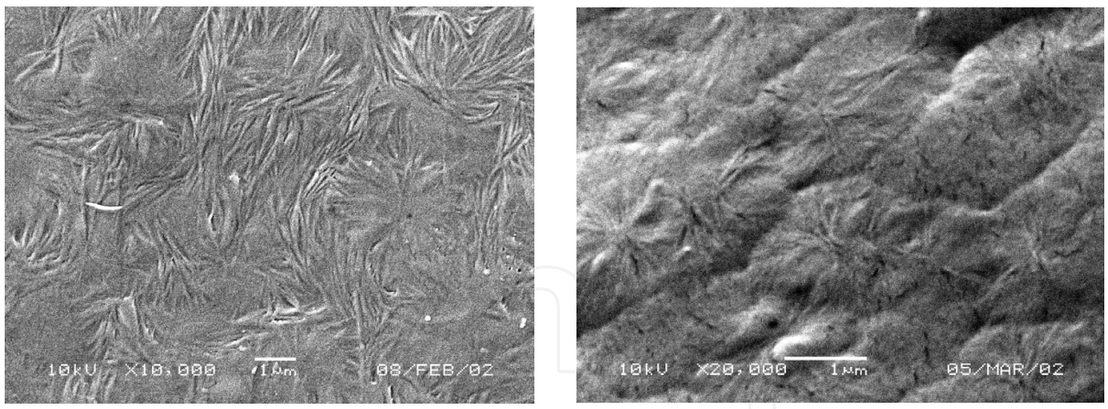
Table 1. Structural parameters of fibres coloured with quinacridone pigment

In fibres the relatively high amount of β crystals is formed already at low pigment concentration. For fibres containing 0.1% of pigment the K value achieves relatively high value of 0.76. With the increase of the pigment concentration until 0.5% the β form content successively increases. For the pigment concentration of 0.3% and 0.5% the *K* value grows to 0.89 and 0.95, respectively. Similar high K value is observed for different extrusion temperature, 210, 225 and 250 °C (Broda, 2004c).

The K value observed in fibres coloured with quinacridone pigment is comparable to the value obtained during crystallization of polypropylene melt in quiescent conditions in the presence of very effective β nucleating agents.

The appearance of β crystals in the coloured fibres taken at low velocity is a result of the ability of quinacridone pigment to nucleate β modification of polypropylene and appropriate crystallisation conditions. During formation of fibres at low take-up velocity the crystallisation occurs at low cooling rate and low molecular orientation. In these conditions, during solidification of fibres, pigment takes part in the nucleation process. The crystallisation proceeds on heterogeneous nuclei produced with the participation of pigments. As a result of the crystallisation fine spherulitic structure is formed (Fig.4) (Broda, 2003c).

The low cooling rate favours the formation of the β form of polypropylene (Huang et al., 1995). The crystallization process starts at the relatively high temperature, above the lower critical temperature for the formation of the β modification (Lovinger et al., 1977). As a result of the epitaxial growth on the surface of quinacridone crystals, the crystals of β modification are formed. At this temperature, the growth rate of β crystals exceeds the growth rate of α crystals (Varga, 1989). The β nuclei formed on the surface of pigment crystals quickly grow forming the high amount of β crystals.



a) b)

Fig. 4. Spherulitic structure of fibres coloured with quinacridone taken at very low velocity: a) gravity spun ; b)100 m/min.

In the fibres taken at higher velocities the crystalline structure changes. With the increase of the take-up velocity the content of the β form rapidly decreases. For fibres extruded at 210°C taken at 200 m/min and 300 m/min the K value decreases to 0.47 and 0.09, respectively. For the fibres extruded at higher melt temperature 250 °C the decrease of the β form content is even higher. For fibres taken at 200 m/min and 300 m/min the K value drops to 0.33 and 0.08. In the same time the content of the α form increases and the crystallinity index does not change significantly.

The increase in take-up velocity and the extrusion temperature results in the increase of the cooling rate. Consequently, the crystallization temperature moves toward lower values. The crystallization starts at lower temperature and then quickly, by further cooling, moves below the critical temperature for the formation of β crystals. Then, the smaller part of the material crystallizes at conditions favourable for the formation of the β form. At the beginning of the crystallization process β crystals are formed. During crystallization temperature decreases into the range below the critical temperature and remaining crystallisable material crystallizes at a lower temperature, forming α crystals.

In temperature below the low critical temperature the growth rate of α crystals is higher than the growth rate of *β* crystals (Fillon et al., 1993). Then α nuclei grow quickly, while the growth of the *β* nuclei is strongly constrained.

With the increase in take-up velocity, the temperature is lower and lower, and less and less material can crystallize at a temperature above the critical temperature for the formation of β crystals. With the increasing take-up velocity more and more material crystallize at lower temperatures and β form content decreases.

For the fibres taken at medium velocities, from 400 to 1050 m/min only the minimal content of β crystals is formed. The crystalline structure is built almost exclusively from the α crystals. In the fibres produced without pigments at the same conditions the high mesophase content was observed (Broda, 2004a). This fact suggests that at medium take-up velocities the quinacridone pigment induces the formation of α crystals. The investigations of Rybnikar (Rybnikar, 1991) and Mathieu (Mathieu et al., 2002) showed that *γ* quinacridone reveals a versatile nucleating ability and may induce either α or *β* modification of

polypropylene. The versatile nucleating ability of the quinacridone pigment results from the fact that the spacing between the grooves on the *bc* surface of *γ* crystal is similar as well to the interchain distance of the isochiral helices in the (010) plane of the α form of polypropylene. By the arrangement of polypropylene helices parallel to the grooves the nearly perfect match between above-mentioned dimensions may be achieved and the epitaxial growth of α crystals may be initiated.

By further increase of the take-up velocity the structure with the high content of well oriented α crystals is formed. It is know that during formation of fibres at high velocities the molecular orientation has a great influence on the polymer crystallization. Under high molecular orientation certain chain segments become aligned. Bundles of aligned segments form so called row nuclei, which initiate lamellae growth in the perpendicular direction. At high velocities a big number of row nuclei is formed. In this condition the heterogeneous nucleation on pigments loses its importance. The nucleation proceeds without the participation of pigments. Crystals of pigment do not participate in the formation of row nuclei and do not disturb their formation. Relatively small amount of pigment does not affect the mobility of polypropylene chains and does not influence the growth of polypropylene crystals. The growing polypropylene crystals push out pigment outside crystals to the amorphous regions.

The crystallisation in coloured fibres occurs at the same rate and at the same temperature as in non-coloured fibres. The lamellar crystals formed on the row nuclei alternate with the amorphous areas forming fibrillar structure (Broda, 2004b). The long period for coloured fibres determined on Small Angle X-Ray Scattering (SAXS) measurements equals 10.6 nm and has the similar value as in the case of non-coloured fibres (Broda, 2003b).

4.2 Structure of fibres coloured with phthalocyanine pigment

The values of the crystallinity index and K value for fibres coloured with phthalocyanine pigment calculated on the basis of WAXS measurements are presented in Table 2.

Extrusion temperature [°C]	Take-up velocity [m/min]	Crystallinity index	K value
210	100	0.57	0.31
	200	0.56	0.14
	300	0.53	-
	400	0.51	-
	880	0.42	-
	1050	0.43	-
	1350	0.52	-
250	100	0.54	0.29
	200	0.52	0.09
	300	0.44	-
	400	0.40	-
	880	0.36	-
	1050	0.31	-
	1350	0.36	-

Table 2. Structural parameters of fibres coloured with phthalocyanine pigment

For fibres taken at low take-up velocity 100 m/min the high crystalline structure is formed. The cristallinity index reaches high value of 0.57. The crystalline structure is built mainly from α crystals with an addition of β crystals. The content of the β crystals characterised by the K value equals 0.31.

Similarly as for fibres coloured with quinacridone at low take-up velocity, phthalocyanine participates in the nucleation process. The crystallisation starts on heterogenous nuclei formed on the crystals surface. The numerous nuclei grow forming fine spherulitic structure.

Phthalocynine is known as efficient nucleating agent of the α form of polypropylene. The high crystalline structure of the fibres results from its high nucleation ability. Appearance of the small number of β crystals is surprising.

The ability to nucleate β crystals can be explained by the surface geometry of phthalocyanine crystals. For α modification of the phthalocyanine the distance between grooves on the lateral surfaces equals 1.19 nm (Honigmann et al. 1965). This dimension is comparable with the spacing of 1.1 nm between helices of the same hand in the trigonal cell of the β form of polypropylene.

The compatibility of these dimensions is responsible for a good nucleating ability toward the β form of several calcium dicarboxylates (Li et al., 2002) and may also explain the formation of a certain amount of β crystals in fibres coloured with phthalocyanine.

With the increase of the take-up the content of β crystals rapidly decreases. For fibres taken at take-up velocity 200 m/min and extruded at 210 °C and 250 °C the *K* value drops to 0.14 and 0,09, respectively. At higher velocities β crystals are not observed.

At higher cooling rates the crystallization conditions for formation of the *β* form are less favorable. On the surface of the phthalocyanine pigment only α nuclei are formed. The growth of nuclei leads to formation of the high crystalline structure built only from α crystals.

Similarly to fibres coloured with quinacridone at high take-up velocity above 1000 m/min, pigment does not participate in the nucleation process. In these conditions, under high molecular orientation numerous row nuclei are formed. Row nuclei quickly grow forming well oriented lamellar α crystals. In fibres the fibrillar structure is formed (Fig.5)

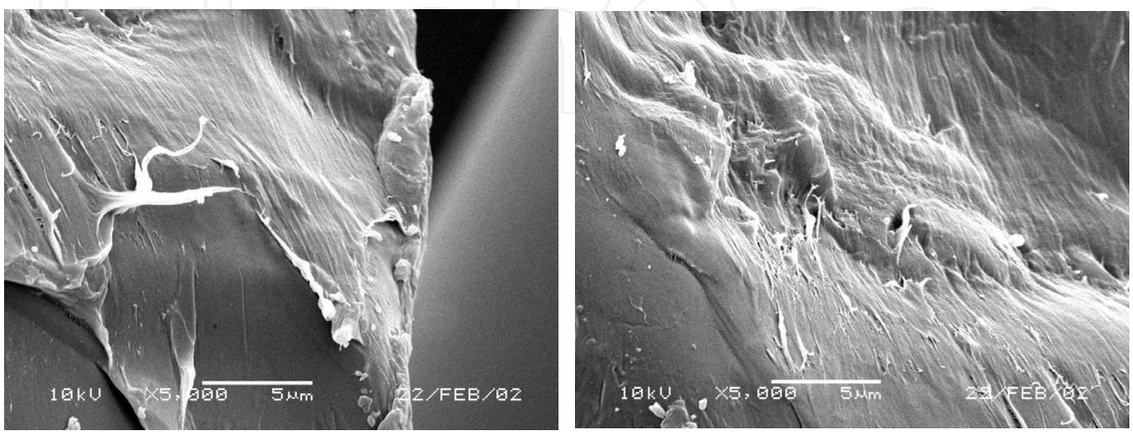


Fig. 5. Fibrillar structure in fibres coloured with phthalocyanine taken at 1350 m/min.

4.3 Structure of fibres coloured with the mixture of quinaridone and phthalocyanine pigments

Mixing of pigments is the common procedure for achieving different colour effects. By mixing of qunacridone and pthtalocyanine two pigments with different efficient nucleating ability toward polypropylene crystallisation are introduced. One can expect that by mixing of both pigments a competition between formation of α and β nuclei will be observed. Such competition, together with a different growth rate of both forms, should lead to formation of a structure with different constitution.

Table 3 presents structural parameters determined on the WAXS measurements for fibres coloured with the 1:1 mixture of quinacridone and phthalocyanine.

Take-up velocity [m/min]	Crystallinity index -	K value -
100	0.53	0.75
200	0.53	0.52
300	0.53	0.14
400	0.51	0.05
880	0.52	0.04
1050	0.51	-
1350	0.52	-

Table 3. Structural parameters of fibres coloured with the mixture of quinaridone and phthalocyanine pigments

At the lowest velocity 100 m/min inside fibres the crystalline structure consisting of both polymorphic modifications is formed. The K value equals 0.75. The content of β crystals is much higher than the content of α crystals. Nevertheless, the content of the β form is much lower in comparison to fibres coloured with quinacridone alone, but significantly greater in comparison to fibres coloured with phthalocyanine (Broda, 2003d).

In fibres taken at very low velocities pigments participate in the formation of the crystallization nuclei. By coloration with the mixture of pigments, both pigments reveal their nucleating activity. On the surface of the quinacridone the β nuclei, while on the surface of phthalocyanine crystals the α nuclei, are formed.

Different content of both modifications in the fibres may be caused by a different number of produced nuclei and/or different rate of crystals growth.

By even proportion of both pigments and their similar dispersion one can assume that the number of the quinacridone crystals equals the number of the phthalocyanine crystals. Both pigments reveal their nucleating activity at similar temperature and formation of α and β nuclei occurs at similar conditions. Taken into account the above mentioned statements, there is no indication of significantly greater number of the β nuclei. The higher content of the β crystals in the fibres coloured with the mixture of pigments have to result from the higher rate of crystals growth.

During formation of fibres at low velocity the crystallization occurs at high temperature. The crystallization temperature exceeds the critical temperature for the formation of the β form. In temperature above critical, the growth rate of the β form crystals exceeds the growth rate of the α crystals (Lovinger et al., 1977). Due to higher growth rate, the β crystals grow quicker and even by equal number of both nuclei form the structure with the high content of the β form crystals.

For fibres formed at higher velocities the crystallization conditions prefer the formation of the α form crystals. Similarly as for fibres coloured with quinacridone, the content of the β form rapidly decreases.

Similarly as for fibres coloured with particular pigments at high velocities, the mechanism of the nucleation changes. The crystallization proceeds without pigments on row nuclei formed under high molecular orientation. As a result, in all fibres the structure consisting of the α modification characterized by the same crystallinity index and the same lamellar thickness is produced.

5. Influence of processing on the structure of polypropylene fibres coloured with quinacridone pigment

To achieve final properties, as-spun fibres obtained by the spinning line are usually submitted to further processing. During processing the fibres structure formed by spinning undergoes further transformation. Heat stabilisation and drawing are of a great importance. Both treatments strongly affect the structure of the fibres and their final properties.

During heat stabilisation of as-spun fibres coloured with quinacridone pigment the less thermodynamically stable β crystals transform into α crystals.

In the case of fibres extruded at the lowest velocity exhibiting the highest amount of β crystals the first changes of the content of β form are observed at heating at 140°C. The amount of β crystals decreases already after 3 minutes of stabilization. For longer time decrease of the β form content is more pronounced. The K value decreases from 0.95 for not stabilized fibres to 0.63 for fibres stabilized for 5 minutes. After a very long time the high amount of β crystals remains unchanged. For the fibres stabilized at higher temperatures, in the range 140–148°C, the β form content gradually decreases with the increment of the stabilization temperature. The content of the β form decreases quickly during the first minutes of heating. For longer times of heating (up to 10 min) further changes of the β form content are less meaningful. After certain time the β→α transition stops. Despite the long time of stabilization the content of β crystals does not change. During stabilization at 150°C a rapid drop of the β form content is observed already after 3 minutes of heating. In this time the K value drops to 0.1. Then, after 10 minutes the β crystals disappear (Broda, 2004d).

The transition of the polymorphic forms of polypropylene was observed many times. It was stated that the β→α transition is not reversible and occurs in the temperature range of 130 to 150°C (Forgacs et al., 1981; Varga, 1995). For years several mechanisms of the transition have been proposed. Garbarczyk suggested that the β→α transition proceeds in a solid state in three intermediate stages based on rotations and translations of polypropylene chains (Garbarczyk, 1985, 1989). Due to considerable differences in unit cells of both modifications, Samuels stated that the β→α transition must take via the liquid phase (Samuels & Yee,

1972). The investigations of Vleeshouwers confirmed that the transition is connected to the melting of β crystals (Vleeshouwers, 1997). Zhou proved that the melting of β crystals occurs partially, starting from the less perfect crystals possessing the lowest melting temperature (Zhou et al., 1986). Rybnikar suggested that new α crystals are formed on the lateral faces of the remaining thickened β lamellae by regular, probably epitaxial, overgrowth (Rybnikar, 1991). Varga and Fillon stated that the transition can be attributed to the formation of α nuclei within the β crystals during secondary crystallization at temperatures below 100°C (Varga, 1986; Fillon et al., 1993).

Taking into consideration the above mentioned statements, one can conclude that the changes of the β form content in fibres with quinacridone results from the melting of β crystals and their recrystallisation into α crystals. At temperatures near 140°C only a small fraction of the less perfect β crystals is melted. After the melting of such crystallites the transition stops in spite of the long time of stabilization. At higher temperatures, closer to the melting point of β crystals the greater part of the β lamellae is melted and the transition proceeds further. At 150°C, the temperature above the melting temperature of β crystals, all β lamellae melt and recrystallize, forming α crystals. At this temperature the β→α transition is completed within few minutes.

The changes, which occur in the fibres' structure during drawing depend on drawing temperature. During drawing at room temperature the crystalline structure with the high content of β crystals transforms into mesophase. The significant changes are observed already at draw ratio of 2. At this draw ratio the β form content drops to half of the value for undrawn fibres. With the increase of the draw ratio the transition from crystalline structure to mesophase proceeds further and the content of the β form gradually decreases. At draw ratio of 7 all crystalline structure transforms into mesophase and β crystals disappear.

During drawing at 120°C the gradual transition from β form to α form is observed. As a consequence the β form content in fibres gradually decreases. At draw ratio of 2 the *K*-value drops to 0.45. At higher draw ratios of 3 and 5 it drops to 0.07.

The transition of β crystals into mesophase generated by drawing at room temperature results from pulling polypropylene chains from the lamellar crystals (Ran et al. 2001). As a result, partial destruction of the crystals is observed. Due to limited molecular mobility at room temperature, chains pulled from the crystals aggregate into bundles with no specific arrangement of helical hands. Such bundles, representing a collection of helical segments with a random assembly of helical hands, form the mesophase. At low draw ratios only a few chains are pulled out from the crystals. At higher draw ratios the number of pulled chains increases. Consequently, the β form content in drawn fibres gradually decreases, while the mesophase content increases. At higher draw ratios, the regular lamellar structure of β crystals is completely destroyed and the β form disappears.

During drawing at 120°C chains pulled out from polypropylene crystals posses much higher mobility and may form assemblies ready to crystallize into well ordered α form crystals.

6. Conclusions

Organic pigments commonly used for the coloration of polypropylene fibres exhibit nucleating ability toward polypropylene crystallisation. The rough surface of pigments'

crystals enables epitaxial growth of polypropylene. The various geometry of the surface of pigments' crystals ensures matching of polypropylene chains in different way, what leads to the formation of different polymorphic forms of polypropylene. The red quinacridone pigment promotes mainly formation of the β form crystals. On the contrary the blue phthalocynine pigment enables growth of α crystals.

During fibres coloration pigments are added to the polypropylene granulate and mixed with the polypropylene melt. Presence of insoluble pigments' crystals effect the polypropylene crystallisation. The influence of pigments on the structure of fibres reveals at the lowest take-up velocity. Then, pigments participate in the nucleation process. For fibres coloured with quinacridone almost only β crystals are formed. For fibres coloured with phathalocynine the formation of the high crystalline structure containing α crystals with the addition of the small amount of β crystals is observed. For fibres coloured with the mixture of both pigments the structure with α and β crystals is produced.

For higher velocities the cooling rate increases and the crystallisation conditions favour formation of the α form crystals. As a result in fibres coloured with pigments the β form content rapidly decreases.

By further increment of the take-up velocity the nucleation ability of pigments does not influence the polypropylene crystallisation. Inside fibres under high molecular orientation numerous row nuclei are formed. The crystallisation proceeds on row nuclei without pigments.

By processing of fibres with high content of β form crystals transitions: β→α and β→mesophase are observed. The direction and range of transition depends on the processing parameters.

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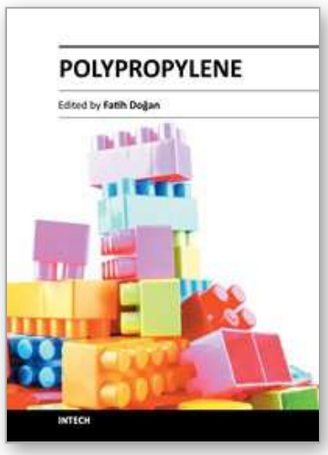
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Polypropylene

Edited by Dr. Fatih Dogan

ISBN 978-953-51-0636-4
Hard cover, 500 pages
Publisher InTech
Published online 30, May, 2012
Published in print edition May, 2012

This book aims to bring together researchers and their papers on polypropylene, and to describe and illustrate the developmental stages polypropylene has gone through over the last 70 years. Besides, one can find papers not only on every application and practice of polypropylene but also on the latest polypropylene technologies. It is also intended in this compilation to present information on polypropylene in a medium readily accessible for any reader.

How to reference

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