

Jan Broda,  
Andrzej Gawłowski,  
Janusz Fabia,  
Czesław Ślusarczyk

# Supramolecular Structure of Polypropylene Fibres Modified by Additives

Institute of Textile Engineering  
and Polymer Materials  
University of Bielsko-Biala  
ul. Willowa 2, 43-309 Bielsko-Biala, Poland  
jbroda@ath.bielsko.pl

## Abstract

*The most common procedure for the modification of polypropylene fibre involves adding additives, which are incorporated into polymer by physical means during fibre formation. Particles of the additives blended with polypropylene melt cause a change in the structural parameters of the fibres. The influence of flame retardants and pigments has been investigated. It was stated that the effect of additives on the fibre structure is based on two mechanisms. The first mechanism is encountered for flame retardants, which do not reveal a nucleating ability toward polypropylene crystallisation. Fibre formation flame retardants affect the melt viscosity and consequently molecular orientation. As a result, a more ordered structure is formed. Contrary to flame retardants, pigments reveal a nucleating ability toward polypropylene crystallisation. During fibre formation low extrusion velocity pigments participate in the nucleation process. Then a high crystalline structure is formed in fibres. At higher take-up velocities the crystallisation process is dominated by a high molecular orientation and the heterogeneous nucleation on pigments loses its importance.*

**Key words:** polypropylene fibre, supramolecular structure, crystallisation, flame retardant, pigment.

So far a wide range of additives, such as pigments, UV stabilisers, flame retardants, antimicrobial and antifungal agents have been used [1]. Recently, intensive investigations into the application of nano-particles have been carried out. By decreasing the size of particles, the effectiveness of additives increases. As a result the concentration of additives can be reduced. Moreover, nano-particles can be easier incorporated into fibres. Some examples of the application of nano-particles include PP/carbon nano-tubes [2], PP/carbon nano-fibres [3], PP/silica [4], PP/TiO<sub>2</sub> [5] or PP/silver [6].

The particles of additives mixed with polypropylene melt occur inside the material during the solidification of the stream and may participate in the crystallisation process, which leads to the formation of fibre structure.

The structure of polypropylene fibres consists of three phases: crystalline, mesomorphic and amorphous. The well-organised crystalline phase is usually built from the most stable monoclinic  $\alpha$  crystals. The second polymorphic form of polypropylene, triclinic  $\beta$ , is more rarely encountered and occurs only in fibres spun in the presence of special nucleating agents [7, 8]. The content of particular phases in fibres varies depending on the formation parameters and may be changed by the addition of additives.

The impact of additives on the structure and properties of polypropylene fibres has been repeatedly investigated [1, 9, 10]. The relation between addi-

tives and fibre structure has also been examined by the Institute of Textile Engineering and Polymer Materials for many years. During these studies the effect of organic pigments and brominated flame retardants was evaluated and the mechanism of their impact was revealed. The Presented herein is a summary of our previous results. [8, 11 - 14, 18]

## Experimental

### Samples

Investigations were carried out for polypropylene fibres coloured with two organic pigments and fibres modified with two brominated flame retardants. Fibres were formed in laboratory conditions using a Brabender screw extruder coupled to a five-hole spinneret die of diameter 0.2 mm. Granules of polypropylene were mixed with additives immediately before fibre formation. Blends of polypropylene and additives were melted and compounded in the barrel of the extruder and then spun into the air. Fibres were extruded from the melt at 210 °C at a constant throughput rate and were taken at different take-up velocities.

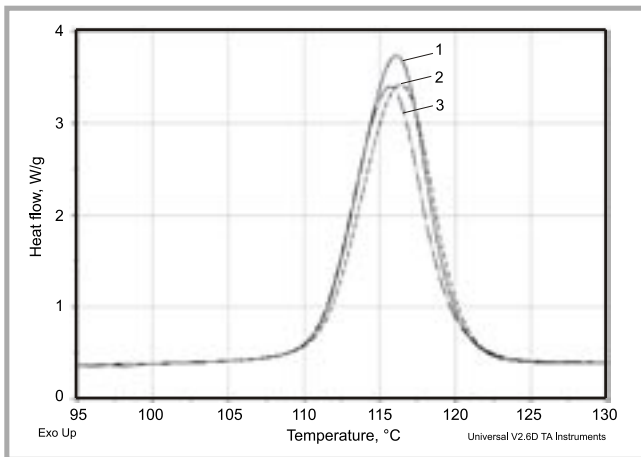
Fibres coloured with quinacridone (C.I. Pigment Violet 19) and phthalocyanine (C.I. Pigment Blue 15) pigments were obtained. Commercial isotactic polypropylene Mosten 52.945 (Chemopetrol, Czech Republic) was used. Pigments were added at a concentration of 0.5 wt% [11, 12].

The second series of fibres were modified with two brominated flame retardants: tris(bromoneopentyl)phosphate and

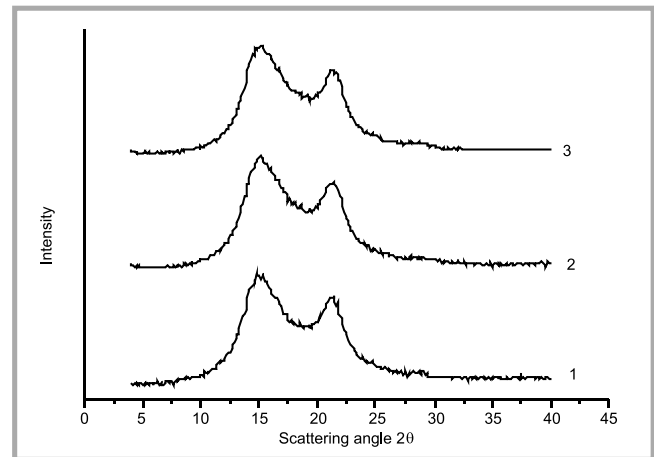
## Introduction

For the last two decades rapid development of polypropylene fibres has been observed. Due to low density, high tensile strength, excellent chemical and biological resistance, low cost and easy processing, polypropylene fibres are widely used in various technical and textile applications.

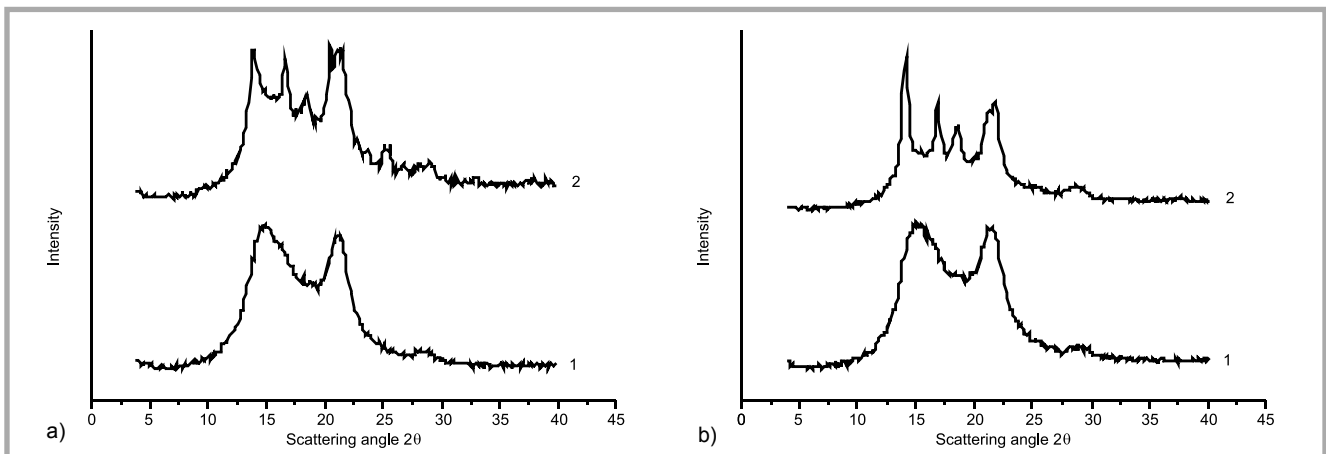
In many cases the properties of row polypropylene fibres do not satisfy special requirements and their modification is required. The most common procedure for the modification of polypropylene fibre involves adding additives, which are incorporated into polymer by physical means during fibre formation. The particles of the additives are blended with polypropylene granulate or they are incorporated directly into polymer melt during fibre formation.



**Figure 1.** DSC curves for polypropylene cooled at 10 K/min; 1) polypropylene, 2) polypropylene + tetrabromobisphenol A bis (2,3-dibromopropyl ether) (5%), 3) polypropylene + tris (bromoneopentyl) phosphite (5%);



**Figure 2.** WAXS patterns for fibres taken at 100 m/min; 1) polypropylene; 2) polypropylene + tris (bromoneopentyl) phosphite (5%); 3) polypropylene + tetrabromobisphenol A bis (2,3-dibromopropyl ether) (5%).



**Figure 3.** WAXS patterns for fibres taken at 200 m/min; a - fibres modified with tris (bromoneopentyl) phosphite taken at 200 m/min; retardant concentration: 1) 3%; 2) 5%; b - fibres modified with tetrabromobisphenol A bis (2,3-dibromopropyl ether); retardant concentration: 1) 5%; 2) 10%;

tetrabromobisphenol A bis (2,3 – dibromopropyl). In this case commercial isotactic polypropylene Tatren TI 922 (Slovnaft, Slovakia) was used. A series of fibres with various amounts of the flame retardant (3, 5 and 10 wt%) were obtained [13].

## Methods

The influence of pigments and flame retardants on the crystallisation process of polypropylene in quiescent conditions was estimated by means of the differential scanning calorimetry (DSC). The investigations were carried out using the analytical system TA Instruments with an MDSC 2920 calorimeter equipped with a Refrigerated Cooling System. By comparison of the crystallisation temperatures of pure polypropylene and polypropylene containing additives, the nucleating efficiency of additives was evaluated [14].

The supermolecular structure of fibres was evaluated by the wide-angle X-ray scattering (WAXS) method using an HZG 4 X-ray diffractometer and Seifert. A diffraction pattern analysis was carried out using an OptiFit computer program [15]. On the basis of the diffraction patterns, the crystallinity index and the mesophase content were calculated.

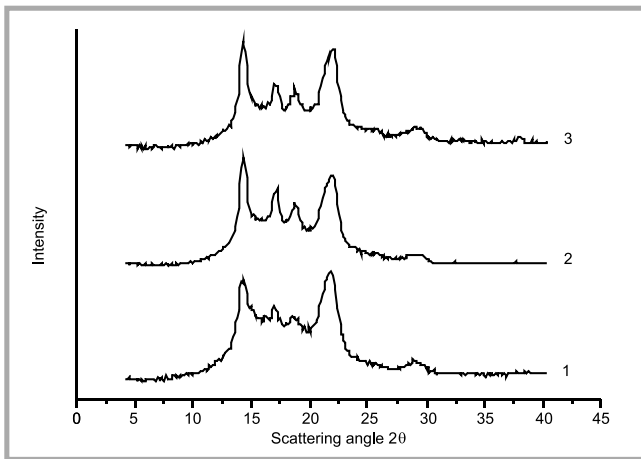
## Results and discussion

### Flame retardants

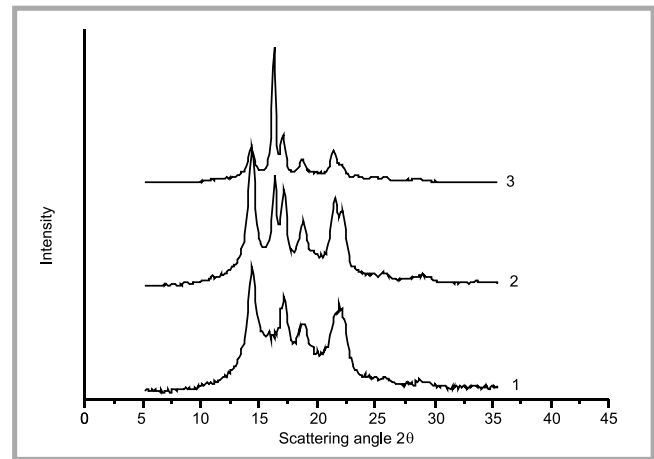
Figure 1 presents the DSC cooling curves for the polypropylene crystallised in quiescent conditions. On the thermogram a single exotherm corresponding to the crystallisation process is observed. For the pure polypropylene the crystallisation temperature equals 116 °C. For polypropylene containing flame retardants the shape of the thermogram and the peak

position does not change. The crystallisation temperature of the polypropylene melt containing tris (bromoneopentyl) phosphite and tetrabromobisphenol A bis (2,3-dibromopropyl ether) equals 116.4 °C and 115.7 °C, respectively. The lack of change the crystallisation temperature means that the flame retardants used do not reveal a nucleating ability toward polypropylene crystallisation.

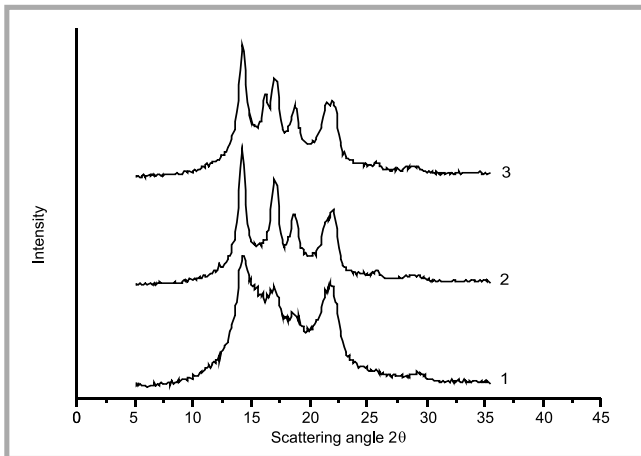
During fibre formation flame retardants incorporated into polypropylene influence the fibre structure by certain formation parameters. Figure 2 presents a series of WAXS patterns obtained for fibres taken at very low take-up velocity 100 m/min. For all fibres, independent of the addition of retardants, two similar broad mesophase peaks are observed. In unmodified and modified fibres a similar structure with a high mesophase content is formed.



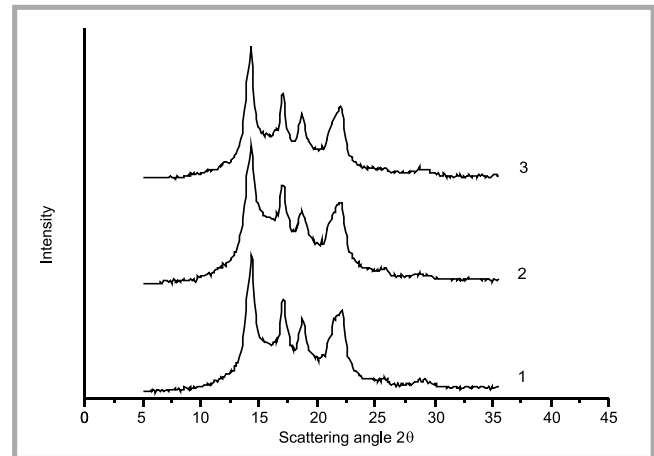
**Figure 4.** WAXS patterns for fibres taken at 1350 m/min; 1) polypropylene; 2) polypropylene + tris (bromoneopentyl) phosphite (5 %); 3) polypropylene + tetrabromobisphenol A bis (2,3-dibromopropyl ether) (5 %)



**Figure 5.** WAXS patterns for coloured and uncoloured polypropylene fibres taken at 100 m/min; 1) uncoloured fibre, 2) fibre coloured with phthalocyanine pigment (0.5%), 3) fibre coloured with quinacridone pigment (0.5%).



**Figure 6.** WAXS patterns for coloured and uncoloured polypropylene fibres taken at 300 m/min; 1) uncoloured fibre, 2) fibre coloured with phthalocyanine pigment, 3) fibre coloured with quinacridone pigment.



**Figure 7.** WAXS patterns for coloured and uncoloured polypropylene fibres taken at 1350 m/min; 1) uncoloured fibre, 2) fibre coloured with phthalocyanine pigment, 3) fibre coloured with quinacridone pigment.

In the case of fibres taken at the higher velocity of 200 m/min and with a small amount of retardants, WAXS patterns with broad mesophase peaks are obtained. The pattern is similar to the one obtained for unmodified fibres. At a higher retardant concentration on the pattern, easily distinguished crystalline peaks appear. An increase in the intensity of crystalline peaks is observed for fibres containing tris (bromoneopentyl) phosphite (Figure 3.a) and tetrabromobisphenol A bis (2,3-dibromopropyl ether) (Figure 3.b) due to the increment of the retardant concentration. The changes in the patterns observed show that for higher concentrations of retardant the content of the crystalline phase in polypropylene fibres increases.

At the highest take-up velocity 1350 m/min, for all the fibres extruded with and with-

out retardants on the patterns, strong crystalline peaks are observed (Figure 4). In all the fibres, with and without flame retardants, the same crystalline structure is formed.

The change in fibre structure resulting from the addition of flame retardants is caused by their influence on the melt viscosity [16]. During the formation of fibres at very low take-up velocity, the crystallisation process is governed by the cooling rate and is not dependent on the melt viscosity [17]. In this case the addition of flame retardants does not impact the fibre structure. At higher take-up velocities the higher shear induces the orientation of the polymer molecules in the flow direction. As a natural consequence of this process certain chain segments of polymer molecules become aligned. A bundle of aligned chain seg-

ments forms primary nuclei, which join surrounding polymer molecules and grow perpendicularly, forming lamellae crystals. The degree of orientation from the initial random coil conformation and the extent of their alignment depends on the shear which is directly correlated to the melt viscosity.

As a result of the addition of flame retardants, especially at higher concentration, the melt viscosity increases [16]. Consequently, by spinning the molecular orientation inside, the extruded stream increases. Hence, the crystallisation process proceeds at higher orientation and leads to the formation of a more ordered structure.

At the highest velocity inside the stream, irrespective of the addition of flame retardants, the molecular orientation is

high and a large number of row nuclei are formed. Then the crystallisation process proceeds very quickly and leads, in both cases, unmodified and modified fibres, to the formation of a high crystalline structure.

### Pigments

For polypropylene containing pigments, typical DSC thermograms with single exotherm are observed. Phthalocyanine and quinacridone pigments added to polypropylene melt shift the peak of crystallisation toward a higher value. The increment of the crystallisation temperature for quinacridone and phthalocyanine pigments equals 14.5 K and 13 K, respectively. The considerable increment of the crystallisation temperature testifies to the high nucleating efficiency of pigments.

In fact pigments exhibit high thermal stability and inside polypropylene melt they occur in a crystalline state. During polypropylene crystallization particles of pigments provide a foreign surface reducing the free energy of the formation of a new polymer nucleus.

Phthalocyanine and quinacridone pigments crystallize forming different crystal modifications, which reveal surfaces enabling the epitaxial growth of polypropylene crystals [18]. The various geometry of the contact surface can lead to the formation of different polypropylene modifications. Quinacridone pigment is well known as efficient nucleating agent of the  $\beta$  form of polypropylene [19, 20].

During fibre formation the influence of pigments on the structure of fibres is mainly revealed by low take-up velocities. On WAXS patterns obtained for fibres taken at 100 m/min, characteristic crystalline peaks are observed (Figure 5). For uncoloured fibres only crystalline peaks characteristic for the  $\alpha$  form of polypropylene are visible. For coloured fibres, besides these peaks, the characteristic peak of the  $\beta$  form appears. In the case of fibres coloured with quinacridone pigment, the  $\beta$  peak possesses very high intensity. The patterns obtained show that in fibres spun at the lowest take-up velocity of 100 m/min, a crystalline structure is formed. For uncoloured fibres the crystalline structure consists of  $\alpha$  crystals. For coloured fibres, besides  $\alpha$  crystals,  $\beta$  form crystals are observed. The high content of  $\beta$  crystals is observed for fibres coloured with quinacridone pigment.

For fibres spun at a higher take-up velocity of 300 m/min, besides crystalline peaks, mesophase peaks are visible on the pattern obtained for uncoloured fibres (Figure 6). For fibres coloured with phthalocyanine pigment the characteristic peak of  $\beta$  form disappears, while for fibres coloured with quinacridone pigment its intensity rapidly decreases. One can conclude that in uncoloured fibres a structure with a certain amount of mesophase is formed. In coloured fibres the mesophase does not occur. In fibres the crystalline structure containing mostly  $\alpha$  crystals is formed.

For the highest take-up velocity of 1350 m/min in all fibres, uncoloured and coloured, only crystalline peaks characteristic for the  $\alpha$  form are visible (Figure 7). In fibres, uncoloured and coloured, a similar high crystalline structure is formed.

Results obtained show that by forming fibres taken at very low velocities, pigments participate in the nucleation process. As a result of the heterogeneous nucleation of pigment crystals, a high crystalline structure is formed in the fibres. In the presence of quinacridone pigment the structure with a high content of the  $\beta$  form is produced. At higher take-up velocities the crystallisation process is dominated by the high molecular orientation and the heterogeneous nucleation on the pigment crystals loses its importance. Under the orientation inside the cooled stream, a great number of row nuclei is formed. Then the crystallisation process proceeds very quickly irrespective of the presence of pigments. As a result, in both uncoloured and coloured fibres a high crystalline structure consisting of  $\alpha$  form crystals is formed.

### Conclusions

Additives added to polypropylene melt during fibres formation affect the fibre structure by certain formation parameters. The interactions between additives and polypropylene melt are based on two different mechanisms.

The first mechanism is encountered for additives, which do not reveal a nucleating ability toward polypropylene crystallisation. In this case changes in fibre structure result from the change in molecular orientation, caused by increased

melt viscosity resulting from the addition of additives.

The second mechanism occurs for substances which reveal a nucleating ability toward polypropylene crystallisation. The influence of these substances is reflected in fibre structure during low formation velocities, when additives participate in the nucleation process.



### References

1. Everaert V.; *Chem. Fibres Intern.* Vol. 54, (2004), p. 192.
2. Bhattacharyya A. R., Sreekumar T. Y., Liu T., Kumar S., Ericson L.M., Hauge R. H., Smalley R. E.; *Polymer* Vol. 44(2003), p. 2373.
3. Kumar S., Doshi H., Srinivasarao M., Park J. O., Schiraldi D. A.; *Polymer* Vol. 43(2002) p. 1701.
4. Huang L., Zhan R., Lu Y.; *J. Rein. Plast. Comp.* Vol. 25(2006) p. 1001.
5. Yang H. Zhu S., Pan N.; *J. Appl. Polym. Sci.* Vol. 92(2004) p. 3201.
6. Jeong S. H., Yeo S. Y., Yi S. C.; *J. Mater. Sci.* Vol. 40(2005) p. 5407.
7. Yu Y. White J. L.; *Polym. Eng. Sci.* Vol. 41 (2001) p. 1292.
8. Broda J.; *J. Appl. Polym. Sci.* Vol. 91 (2004), 1413
9. Spruiell J. E., Lu F. M., Ding Z., Richeson G.; *J. Appl. Polym. Sci.* Vol. 62(1996), p. 1965.
10. Marcincin A.; *Prog. Polym. Sci.* Vol. 27, (2002) p. 853.
11. Broda J.; *J. Appl. Polym. Sci.* Vol. 89, (2003) p. 3364.
12. Broda J.; *Polymer* Vol. 44(2003) p. 1619.
13. Broda J., Gawłowski A., Słusarczyk C., Włochowicz A., Fabia J.; *Fibres & Textiles Eastern Europe* Vol. 13 (2005) No. 5(53) p. 110-113.
14. Broda J.; *J. Appl. Polym. Sci.* 90, (2003), 3957
15. Rabiej M.; *Polimery* Vol. 47(2002) p. 423.
16. Utracki L. A., Luciani A.; *Polypropylene A-Z*, ed. by J. Karger-Kocsis, Kluwer Publishers, Dordrecht 1999.
17. Jinan C.; Kikutani T.; Takaku A.; Shimizu J.; *J. Appl. Polym. Sci.* Vol. 37(1989) p. 2683
18. Broda J.; *Crystal Growth & Design*, Vol. 4 (2004) p. 1277.
19. Stocker W., Shumacher M., Graff S., Thierry A., Wittman J. C., Lotz B.; *Macromolecules* Vol. 31(1998) p. 807.
20. Mathieu C., Thierry A., Wittmann J. C., Lotz, B.; *J. Polym. Sci. Part B. Polym. Phys.* Vol. 40(2002) p. 2504.

Received 15.11.2007 Reviewed 15.01.2008