Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 74 (2007) 508–511

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

The influence of additives on the structure of polypropylene fibres

Jan Broda*, Andrzej Gawlowski, Czesław Slusarczyk, Andrzej Wlochowicz, Janusz Fabia

Institute of Textile Engineering and Polymer Materials, University of Bielsko-Biala, 43-309 Bielsko-Biała, ul. Willowa 2, Poland

---

Abstract

The influence of two organic pigments and two flame retardants on the structure of polypropylene fibres was investigated. It was found that by spinning at low velocities in the presence of pigments a highly crystalline structure is formed. In fibres coloured with quinacridone the rarerly encountered β form of polypropylene was observed. Utilising low take-up velocities, the addition of flame retardants leads to an increase in fibre crystallinity. In the case of fibres formed at higher velocities the influence of additives on fibres structure was less visible. For all fibres, independent of additives, a similar structure containing the α form of polypropylene was obtained.

Keywords: Polypropylene fibre; Structure; Pigment; Flame retardant

---

1. Introduction

The use of additives is a common way to modify polypropylene fibres; with the help of additives, the inherent disadvantages of polypropylene fibres can be minimised and the fibre's properties improved. Commonly, additives are incorporated into the polymer by physical means during fibre formation by mixing the additive with the polypropylene prior to melt extrusion.

It is well known that foreign substances added to a polymer melt strongly influence the crystallisation process. Many substances promote nucleation [1] as a result of which, significant changes in the morphology and the supermolecular structure of the polymer are observed. In several cases, additives result in different polymorphic forms of polypropylene being formed [2].

The influence of additives on the crystallisation process observed in quiescent polypropylene melts does not relate directly to the crystallisation process occurring in fibre formation. By spinning fibres, the crystallisation process occurs in a complex non-isothermal way under varying stress conditions. Under such conditions the crystallisation process depends on the cooling rate and molecular orientation [3]. By spinning at low take-up velocities the crystallisation process is governed by cooling rate whereas at higher velocities, the crystallisation process is dominated by molecular orientation.

The contribution of additives to the crystallisation process that takes place during the formation of polypropylene fibres is not well known. Thus far, only the influence of pigments has been extensively studied [4,5]. The effect of other additives often used for the modification of polypropylene fibres was not investigated.

The work described herein concerns the influence of two organic pigments and two brominated flame retardants on the structure of polypropylene fibres.

2. Experimental

2.1. Samples

Fibres were spun under laboratory conditions using a Brabender screw extruder coupled to a five-hole spinneret die of diameter 0.2 mm. Fibres were extruded from the melt at 210 °C and wound up at different take-up velocities from 100 m/min to 1350 m/min. Two commercial isotactic polypropylene resins namely, *Mosten 52.945* supplied by Chemopetrol (Czech Republic) and *Tatren TI 922* supplied by Slovnaft (Slovakia) were used.

---

* Corresponding author.
E-mail address: jbroda@ath.bielsko.pl (J. Broda).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.10.004

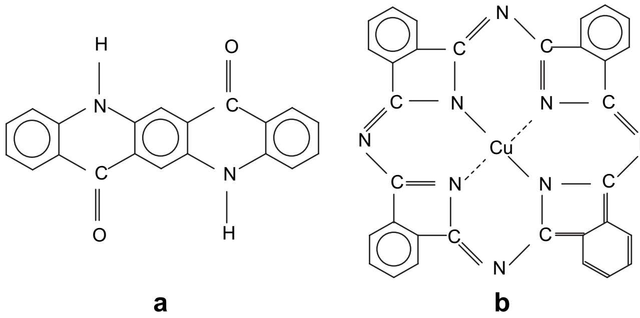

Fig. 1. Chemical formulae of: (a) quinacridone and (b) phthalocyanine.

The structure of coloured fibres as well as fibres modified by brominated flame retardants was compared with the structure of unmodified polypropylene fibres.

For the coloration of fibres quinacridone (C.I. Pigment Violet 19) (Echtrot E3B – Hoechst, Germany) and the phthalocyanine C.I. Pigment Blue 15 (Wola Krzysztoporska – Poland) were used (Fig. 1). Powdered pigments were mixed with the polymer granulate immediately before forming fibres at 0.5% based on polymer mass.

Two commercial retardants, tris(bromoneopentyl)phosphate, *FR-372* (Dead Sea Bromine Group, Israel) and tetrabromobisphenol A bis(2,3-dibromopropyl ether), *PE-68* (Great Lakes, USA) were used (Fig. 2). The retardant was mixed with the polymer granulate at a concentration of 10% by mass. Blends were homogenised in the barrel of the extruder.

2.2. Methods

The effect of the additives on the crystallisation process of the quiescent polypropylene melt was evaluated under non-isothermal conditions. Investigations were carried out using a TA Instruments MDSC 2920 differential scanning colorimeter equipped with a refrigerated cooling system. Samples of unmodified polypropylene as well polypropylene that contained pigments and flame retardants were melted at 210 °C and kept at this temperature for 10 min. After annealing, the samples were cooled in a nitrogen atmosphere at the rate of 20 K min^{-1}. Thermograms were obtained over the temperature range 210–20 °C. Analysis of the thermograms was carried out using the computer program Universal V2.6D supplied by TA Instruments. From the thermograms, the crystallisation temperature was determined.

Fibre structure was evaluated using wide-angle X-ray scattering (WAXS); powdered samples were analysed using both HZG 4 and Seifert X-ray diffractometers. The diffraction pattern analysis was carried out by calculation of a theoretical curve approximating the experimental data. The theoretical curve was constructed as the sum of functions describing the background scattering, an amorphous halo and crystalline or mesophase peaks. The parameters of the component functions were obtained by minimisation of the sum of squared deviations of the theoretical curve from the experimental curve *t* by means of Rosenbrock's method using the computer program OptiFit [6]. On the basis of the diffraction patterns, the crystallinity index and the mesophase content were calculated.

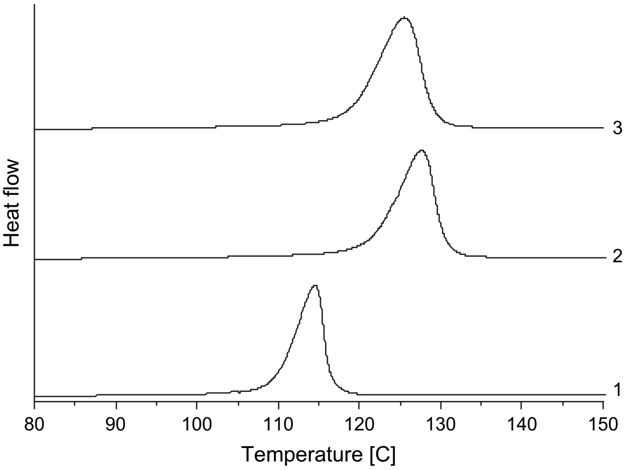

Fig. 3. DSC curves for polypropylene cooled at 20 K min^{-1}. (1) Unmodified polypropylene; (2) polypropylene + quinacridone pigment; (3) polypropylene + phthalocyanine pigment.

3. Results and discussion

3.1. DSC

Fig. 3 shows the DSC cooling curves for both the unmodified polypropylene and the polypropylene that contained quinacridone and phthalocyanine pigments. The crystallisation temperature for the neat polypropylene was 114.5 °C. It is well known that pigments added to the quiescent polypropylene melt shift the crystallisation temperature towards higher values. In the cases of the quinacridone and phthalocyanine pigments, this shift was 14.5 K and 13 K, respectively [7]. The observed increase in the crystallisation temperature shows that both pigments possess nucleating ability towards polypropylene crystallisation. The pigment crystals are insoluble in the polypropylene melt and provide surfaces which can match with the polypropylene chains enabling epitaxial growth of the polypropylene crystals.

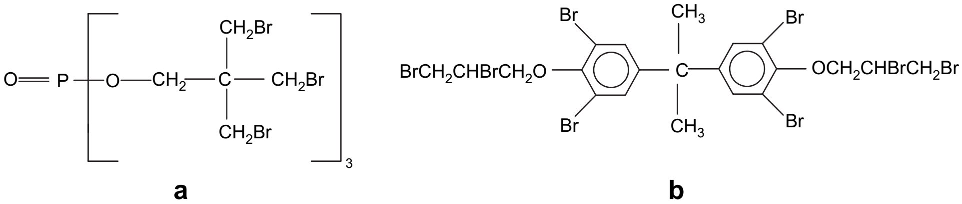

Fig. 2. Chemical formulae of: (a) tris(bromoneopentyl)phosphate and (b) tetrabromobisphenol A bis(2,3-dibromopropyl ether).

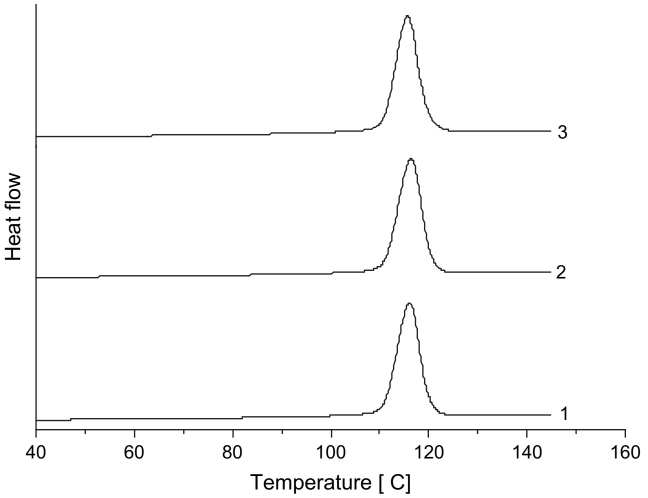

Fig. 4. DSC curves for polypropylene cooled at 20 K min^{-1}. (1) Unmodified polypropylene; (2) polypropylene + tris(bromoneopentyl)phosphate; (3) polypropylene + tetrabromobisphenol A bis(2,3-dibromopropyl ether).

Fig. 4 shows the DSC thermograms for the unmodified polypropylene and polypropylene containing the flame retardants. The crystallisation temperature of the polypropylene melt containing the flame retardants was close to that of the unmodified polypropylene (115.6 °C) from which one can conclude that the flame retardants did not possess nucleating ability. In contrast to the pigments, the flame retardants are soluble in the polypropylene melt. The tris(bromoneopentyl)-phosphate and the tetrabromobisphenol A bis(2,3-dibromopropyl ether) melt at 181 °C and 106–120 °C, respectively. Their solubility in the polypropylene melt prevents their participation in the nucleation process.

3.2. WAXS

Fig. 5 shows a series of WAXS patterns obtained for the unmodified polypropylene fibres. It is evident that the mesophase and the crystalline phase can be distinguished. The content of the meso- and the crystalline-phases varies depending on the take-up velocity. With an increase in take-up velocity the proportion of the mesophase increases. At a take-up velocity of 1000 m/min the mesophase content achieves a maximum value. Above this velocity the mesophase content in the fibre decreases considerably. In fibres obtained at the highest velocity only the crystalline structure is formed.

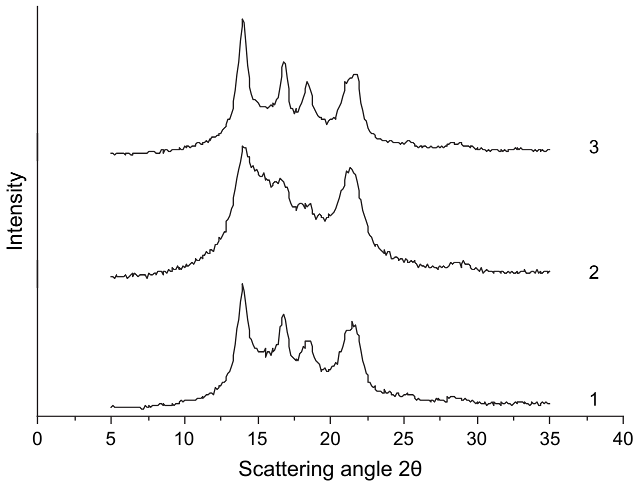

Fig. 5. Series of WAXS patterns measured for neat polypropylene fibres take at different velocities. (1) 100 m/min; (2) 880 m/min; (3) 1350 m/min.

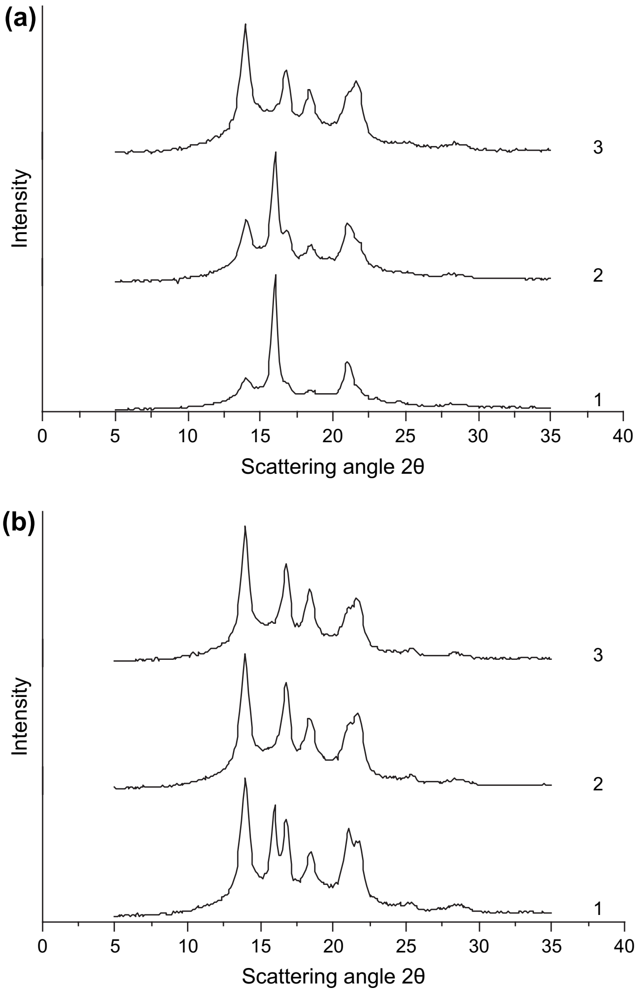

Fig. 6. Series of WAXS patterns for coloured fibres taken at different velocities. (1) 100 m/min; (2) 200 m/min; (3) 1350 m/min. (a) polypropylene + quinacridone pigment; (b) polypropylene + phthalocyanine pigment.

Fig. 6 shows WAXS patterns measured for the coloured fibres. In coloured fibres a semicrystalline structure is formed. The mesophase, which occurs in uncoloured fibres, is not present in fibres containing pigment. At low take-up velocities, fibres coloured with the quinacridone pigment display a high content of the rarely encountered β modification of polypropylene. In the case of fibres coloured with the phthalocyanine pigment the structure consists mostly of the α modification. With an increase in take-up velocity, the content of the β modification in fibres coloured with the quinacridone pigment considerably decreases. At higher velocities in fibres coloured with both pigments, the crystalline structure consists only of the α modification.

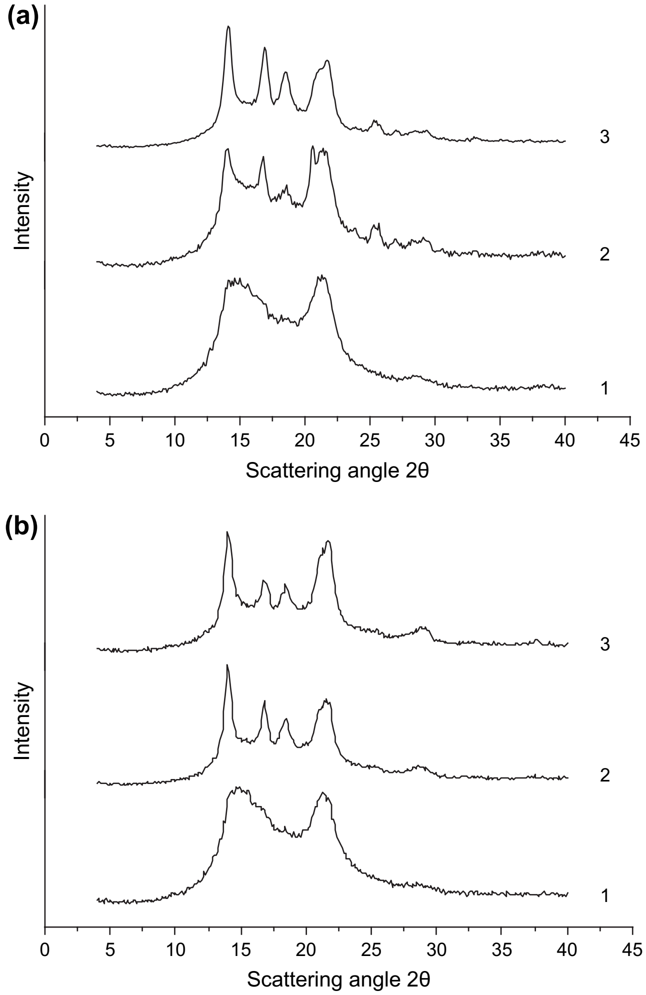

Fig. 7. Series of WAXS patterns for fibres containing flame retardants taken at different velocities. (1) 100 m/min; (2) 300 m/min; (3) 1350 m/min. (a) polypropylene + tris(bromoneopentyl)phosphate; (b) polypropylene + tertrabromobisphenol A bis(2,3-dibromopropyl ether).

The WAXS patterns obtained for fibres modified with flame retardants are presented in Fig. 7. In fibres taken at low velocity, the structure contains a high amount of the mesophase. In the case of fibres modified by the flame retardants, the content of the mesophase is the same as in the unmodified fibres. At higher take-up velocity, the content of the crystalline phase increases considerably. In comparison to unmodified polypropylene fibres, the content of the crystalline phase in fibres modified with flame retardants is significantly higher. In the cases of all fibres extruded both with and without retardants, further increase of take-up velocity results in a concomitant increase in the crystalline phase content.

4. Conclusions

During the spinning of polypropylene fibres, a structure comprising three phases is formed. The proportion of these particular phases, namely the amorphous phase, mesophase and crystalline phase, depends on the formation parameters as well on the kind of the additive used. The effect of additives on fibre structure is more marked at low take-up velocities. Under such conditions, pigments have a nucleating ability towards polypropylene crystallisation. As a result of heterogeneous nucleation on pigment particles that are present in the fibre, a crystalline structure is formed. Flame retardants, which do not have nucleating ability, increase the viscosity of the melt which, during spinning, increases the molecular orientation inside the extruded fibre. Hence, such a crystallisation process results in higher orientation and leads to the formation of a more ordered structure.

The influence of additives on fibre structure at high take-up velocities is less apparent. The influence of heterogeneous nucleation on the pigment crystals as well as the effect of the flame retardants on the melt viscosity loses its importance. At high take-up velocities the crystallisation process is dominated by increased molecular orientation. Inside a cooled stream of poymer, independently of the addition of additives, a great number of row nuclei is formed and the crystallisation process proceeds very quickly giving rise to the α modification of polypropylene.

Acknowledgement

The study was supported by the Polish Committee for Scientific Research – Grant No. 4 T08 E07525.

References

[1] Binsbergen F. Heterogeneous nucleation in the crystallization of polyolefins: part 1. Chemical and physical nature of nucleating agents. Polymer 1970;11:253–67.

[2] Bruckner S, Meille SV. Polymorphism in isotactic polypropylene. Progress in Polymer Science 1991;16:361–404.

[3] Jinan C, Kikutani T, Takaku A, Shimizu J. Nonisothermal orientation-induced crystallization in melt spinning of polypropylene. Journal of Applied Polymer Science 1989;37:2683–97.

[4] Broda J. Morphology of the noncoloured and coloured polypropylene fibres. Polymer 2003;44:1619–29.

[5] Broda J. Polymorphic composition of colored polypropylene fibers. Crystal Growth and Design 2004;4(6):1277–82.

[6] Rabiej M. Determination of the degree of crystallinity of semicrystalline polymers by means of the "OptiFit" computer software. Polimery 2002;47:423–7.

[7] Broda J. Nucleating activity of the quinacridone and phthalocyanine pigments in polypropylene crystallization. Journal of Applied Polymer Science 2004;90:3957–64.