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Effect of Draft Ratio on Crystallinity of Polypropylene/Copolyester Blend Fibers

Abstract
The aim of the research presented is to find the mutual relations between specified structural parameters and selected mechanical properties of iPP/coPES/EVA fibers. The influence of the crystallinity index and lamellar thickness on the mechanical properties of two kinds of modifications of polypropylene fibres (iPP) was studied [1]. The first modification consisted in physical blending of iPP with a specialty copolyester (coPES) in the melt, whereas the second one consisted in adding to the melt a small amount (2% weight) of the ethylene-vinylacetate copolymer (EVA) to improve compatibilisation. The crystallinity index (x), the long period of lamellar structure (L) and the lamellar thickness (L_c) were determined by wide-angle X-ray diffraction (WAXS) and small-angle X-ray scattering (SAXS) measurements. The WAXS investigations were carried out with a URD-65 Seifert diffractometer. The degree of crystallinity was calculated as the ratio of the total area under the resolved crystalline peaks to the total area under the unresolved X-ray scattering curve [2]. The SAXS investigations were performed by means of an MBraun camera, which utilises a conventional Kratky collimation system. An Instron 5544 tensile tester equipped with a Test Profiler-Interface was used to measure the mechanical properties of the investigated fibres. The tests were carried out at two specimen's gauge lengths: of 10 mm between the clamps and at a minimum length near to 0 mm, in order to eliminate the influence of longitudinal dimension. Uniaxial tension tests were performed to obtain the characteristic deformation behaviour, such as modulus of elasticity, proof stress, breaking force and force at rupture. The determination of all the parameters of the modified iPP fibres in relation to the coPES quantity (5¸20% weight) and the technological operations of drawing (R_c=2.6¸4.8) were performed. The modulus of elasticity and breaking tenacity were found to be proportional to the crystallinity index and lamellar thickness for samples of iPP(100%) and samples with a small content of additional coPES particularly. It was also found that the addition of EVA does not improve the correlation coefficient between the mechanical properties and the crystalline structure parameters.

Key words: *polypropylene, copolyester, fibres, supermolecular structure, crystallinity, draft ratio.*

Introduction

This paper presents research on the influence of supermolecular structure on the mechanical properties of modified polypropylene fibres. The aim of the research presented is to establish the mutual relations between the determined structural parameters and selected mechanical properties of iPP/coPES/EVA fibres. The influence of the crystallinity index and lamellar thickness on the mechanical properties of two kinds of modifications of polypropylene fibres (iPP) was studied [1]. Based on tests and analysis of the results of the measurements, we defined the effects of technological drawing and the modifying additives in a fibre on its supermolecular structure.

Experimental

Samples

The modified iPP/coPES/EVA fibres were received by physical blending of isotactic polypropylene (iPP) with a specially synthesised, non-crystallisable co-polyester (coPES) and a co-polymer of ethylene and vinyl acetate (EVA) in the melt. The modifiers were added in order to cause certain changes to the surface and the internal structure of the fibres, which would enable the use of dyeing baths.

The fibres were formed on the extrusion spinning frame with a spinning head equipped with a spinning pump of a capacity of 1.2 cm^3/turn, a side chamber with an air ventilator, and a godet collector constructed at the CInstitute of Chemical Fibres, Łódź, Poland (IWCh) with a winding reel from the Neumag Company.

Drawing the fibres was performed on a SZ-16 draw-twister from Barmag with the options of double-zone drawing (heated godet or heating plate) and a ring twister.

The received fibres had a line mass of 64÷72dtex for all the tested contents iPP/coPES (95/5, 90/10, 85/15 and 80/20), and for the materials including 10 and 20% of weight coPES and 2% of weight EVA. The spinning temperature (261°C) was calculated on the basis of a melt flow index MFI (270°C, 21.2 N, Φ=0.5 mm); the mass efficiency of extrusion was 15.8 g/min, and the take-up velocity was 600 m/min.

The drawing of all the fibres containing coPES (and perhaps EVA as well) pro-

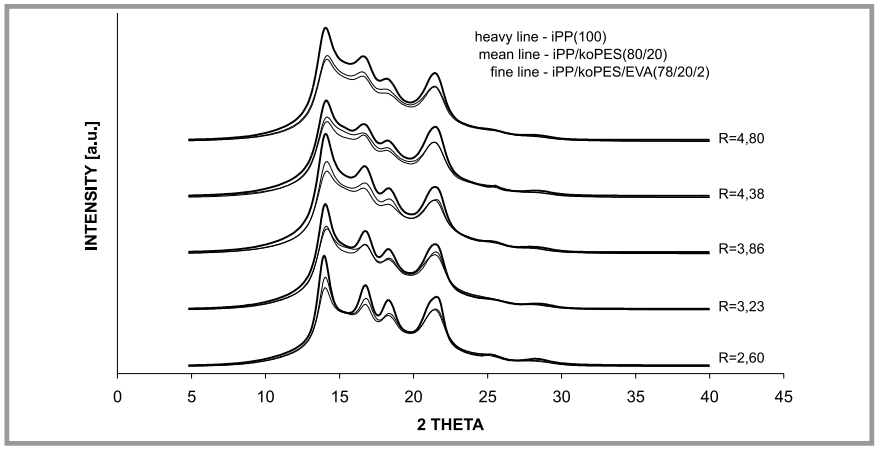

Figure 1. *Comparison of WAXS curves for the different drawn iPP Malen PS702 fibres and modified with 20%w. coPES and compatibiliser EVA.*

ceeded without any disturbances over the whole range of the applied draft ratios (R=2.6÷4.8).

No disturbances were observed during spinning, and the process of drawing proved good processing of the fibres which includes modifiers. The structure of the fibres directly after spinning was convenient to conducting the process of their orientation because they showed susceptibility to deformation such as that in unmodified fibres.

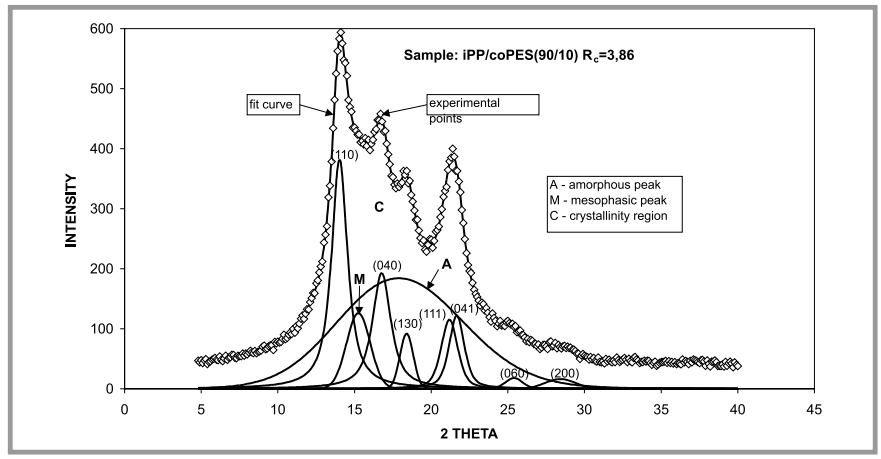

Figure 2. WAXS curve resolved into individual peaks; for example, sample iPP/coPES(90/10) R=3.86. (M – mesomorphic phase diffraction reflexes; A – amorphous phase diffraction reflex). The structure of fibres was created during the formation process and drawing.

Experimental methods

WAXS

Wide-angle X-ray scattering (WAXS) investigations were carried out with a URD-65 Seifert diffractometer. CuK_α radiation was used at 30kV and 20mA. Monochromatisation of the beam was obtained by means of a nickel filter and a pulse-height analyser. A scintillation counter was used as a detector. Investigations were performed within the range of angles 5° to 40° with a step of 0.1°. Each diffraction curve was corrected for polarisation, the Lorentz factor, and incoherent scattering. Determining the content of a crystalline phase in polymers by X-ray methods requires the separation of an experimental diffraction pattern into two components connected with the scattering from the crystalline and amorphous regions respectively. For this purpose, the OptiFit curve-fitting computer package [2] was used.

The degree of crystallinity (χ) was calculated as the ratio of the total area under the resolved crystalline peaks to the total area under the unresolved X-ray scattering curve.

SAXS

Small-angle X-ray scattering (SAXS) investigations were performed by means of an MBraun camera, which utilises a conventional Kratky collimation system. The front of the camera was directly mounted on the top of the tube shield of a stabilised Philips PW 1830 X-ray generator. The X-ray tube was operated at a power of 1.5kW. CuK_α radiation was used; monochromatisation was performed by a Ni β filter and pulse-height discrimination. The entrance slit was adjusted to 50μm. Scattered radiation was recorded at an acquisition time of 900s by means of an MBraun linear position-sensitive detector, model PSD 50. The detector had 1024 channels with a channel-to-channel distance of 52μm.

The experimental SAXS curves were corrected for sample absorption and desmeared from collimation distortions by means of the 3DVIEW computer program supplied by MBraun.

The crystalline long period L, which is related to the distance between lamellae, was determined from the SAXS measurements. The peak position of the SAXS profiles are taken to calculate the average lamellar thickness from:

$$L_c = \chi_{vol} \cdot L$$

where χ_{vol} is the volumetric percentage of crystallinity calculated from the crystal weight percentage χ:

$$\chi_{vol} = \frac{\frac{\chi}{\rho_c}}{\frac{\chi}{\rho_c} + \frac{100-\chi}{\rho_A}} \times 100\%$$

where χ was obtained from the WAXS profiles, ρ_C is the crystal density, and ρ_A is the amorphous density. The val-

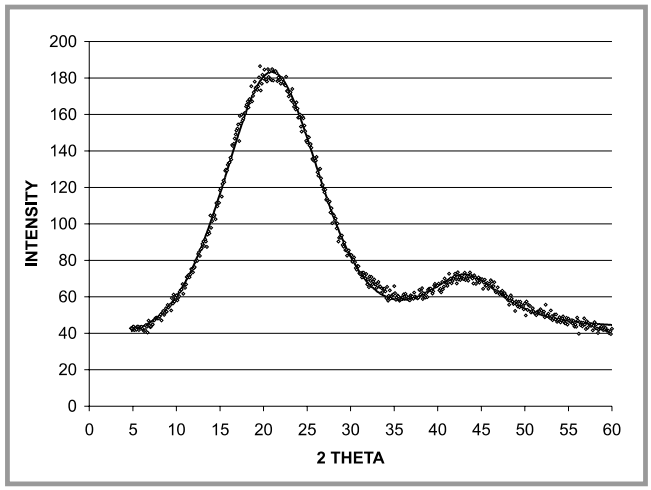

Figure 3. WAXS curves for copolyester coPES; ∘ copolymer coPES, — fit curve.

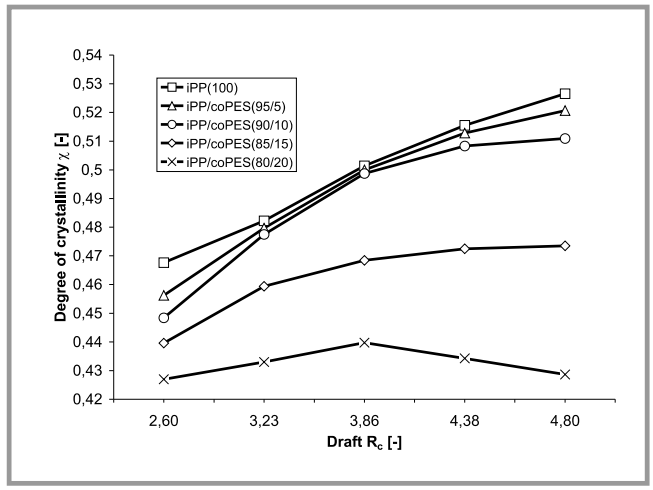

Figure 4. Changes in degree of crystallinity of iPP matrix for modified iPP fibres in function on draft ratio.

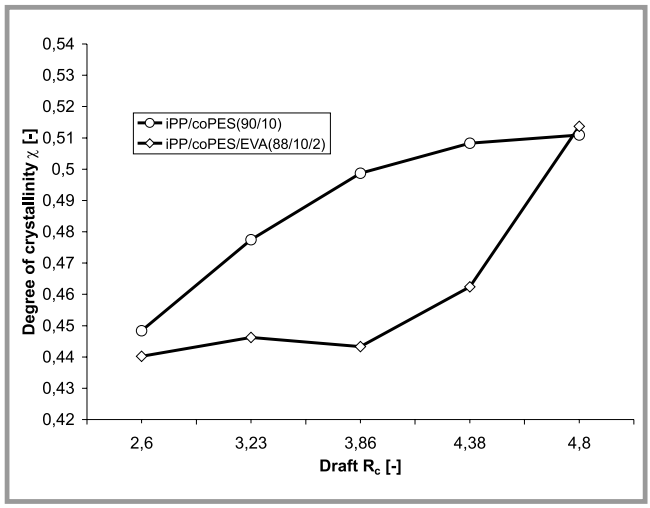

Figure 5. Comparison of changes in degree of crystallinity of iPP matrix for modified iPP fibres with and without EVA as a function of draft ratio.

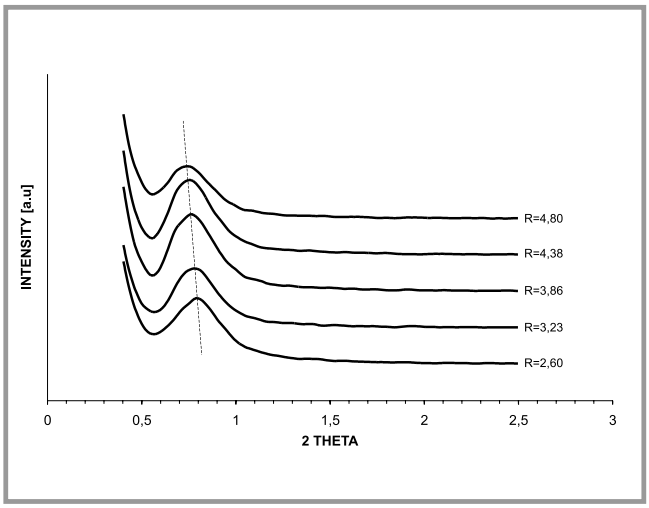

Figure 6. SAXS curves (in the direction parallel to the fibres axes) for the different drawn fibres iPP/coPES(90/10).

ues for the amorphous and crystalline densities where adopted from van Krevelen [3] (for iPP: ρ_C=0.95g/cm^3, ρ_A=0.85g/cm^3).

Mechanical investigations

The tensile strength parameters of the fibres were defined according to the rules of the norm PN-EN ISO 5079 by means of the Instron 5544 Single Column tensile testing machine [4]. The machine consisted of a press-stretching head for fibres of a static load cell rating of ±10N with an indication error of 0.05%. The tensile testing machine was connected to a computer equipped with Merlin software. The samples were placed on the tensile testing machine in frames. During the research, we did not consider any measurements where the fibre was broken directly at the jaws. The measurements were taken in normal climatic conditions for samples of 10 mm in length and for samples with a length close to zero. The tensile speed was 50 mm/min, and 100 tests were made for each sample.

Results

The results of the measurements were analysed in the aspect of the supermolecular structure changes caused by additives and the process of drawing on the mechanical parameters of the tested fibres.

The experimental curve when resolved into individual peaks indicates that the iPP/coPES fibre has relatively low crystallinity with well-formed α-crystals [5, 6]. No other polymorphic forms of PP are observed. The shape of the WAXS pattern is also determined by the diffraction reflexes of the mesophase denoted in Figure 2 as 'M' at 2Θ of about 15°, and also by a distinct wide peak 'A', which qualifies the scattering of the sample's amorphous phase.

By comparison of the WAXS curves obtained for the fibres with different coPES content which we investigated, we may conclude that the increase in the modifier content changes the shape of these curves. The intensity of the peaks from the crystalline planes of iPP of (110), (040), (130), (111), (041) decreases, as does the mesophase. This proportion of diffraction reflex intensities changes when the coPES content continuously grows. The changes mentioned above prove that the total index of order (the sum of the content of crystalline phase and mesophase) calculated in respect to the total amount of samples investigated decreases .

The values of the crystallinity degree of modified iPP/coPES/EVA fibres were calculated only in respect to the iPP matrix (Figure 4, 5)

The comparison of SAXS curves (Figure 6) obtained for the fibres in the direction parallel to the fibre axes shows the existence of the lamellar structure of the iPP matrix [7, 8] in all samples. For example, the long period of this structure for the iPP/coPES(90/10) fibres (calculated from Bragg's law) varies from 115Å to 124Å

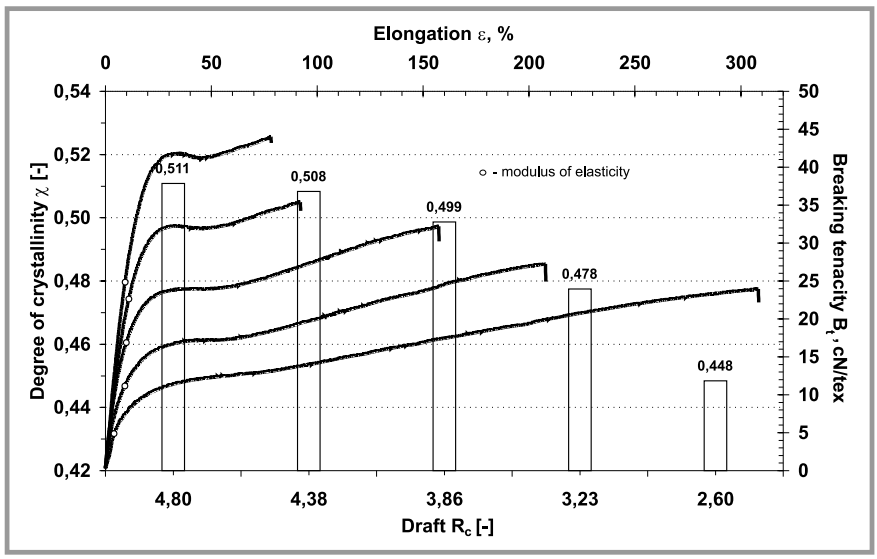

Figure 7. Comparison changes in degree of crystallinity, breaking tenacity and modulus of elasticity as a function of the draft ratio.

for the draft ratio from R=2.6 to R=4.8 respectively.

It was found that the modulus of elasticity and breaking tenacity changed in a distinct manner depending on the applied technological draft ratio R. Their values increase together with the increase in R. By analysing the value of the degree of crystallinity for various values of draft ratio, it was found that they grow together with the growth of drafts. Selected results of calculations for example samples are illustrated in Figure 7.

Conclusions

- The supermolecular structure of studied fibres was created in the same way as classical iPP fibres;
- WAXS studies revealed that besides the a monoclinic form of iPP in fibres, the mesophase of iPP was formed;
- The crystallinity of investigated samples decreases with the increase in additive coPES content, but it increases with the draft increase for drawn fibres (Figure 4);
- The increase of the content of ordered phase (crystalline + mesophase) in the iPP matrix as a function of the draft ratio depends on the addition of EVA compatibiliser (Figure 5);
- SAXS studies in the direction parallel to the fibre axes show the existence of the lamellar order in all samples. The long period of this structure slightly decreases with the increase in the coPES content, whereas it distinctly increases with the increase of the draft ratio (Figure 6).

Acknowledgment

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References

1. *Schrauwen B.A.G., Janssen R.P.M., Govaert L.E., Meijer H.E.H., Macromolecules, (2004), 37, 6072*
2. *M. Rabiej, Fibres and Textiles in Eastern Europe, 11, No. 5(44), 83 (2003).*
3. *Van Krevelen D.W., Properties of Polymers, 3rd ed.; Elsevier: Amsterdam, 1994.*
4. *Technical-motion documentation of the Instron resistance machine, model 5544*
5. *Brukner S., Meille S.V.,Petraccone V., Pirozii B., Prog. Polym. Sci. 1991, 16, 361.*
6. *Martorana A., Piccarolo S., Scichilone F., Macromol. Chem. Phys. 1997, 8, 597.*
7. *Bieliński D., Ślusarski L., Włochowicz A., Ślusarczyk Cz., Douillard A., Polymer International 44 (1997) 161-173.*
8. *Broda J., Ślusarczyk Cz., Włochowicz A., Journal of Applied Polymer Science 73 (1999) 477 - 488.*

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International Conference
'Fibrous Materials – 21st century'

Saint Petersburg, Russia, 23-27 May 2005

The organiser of this event was the St. Petersburg State University of Technology and Design. The conference was a genuinely broad international forum held in Russia. The Conference program included 74 oral presentations and more than 50 posters; they were presented by speakers from 19 countries. More than 300 participants from 22 countries around the world attended the Conference.

Thanks to the selection carried out by the International Organising and Programming Committee, the advanced subject matter of the presentations created great interest in the participants of this event.

The main topics of the conference were research into fibres, textiles, papers, and composites based on them.

The plenary session included the opening Ceremony and the two following presentations:

- **"The Outlook and Future Developments of Technical Textiles and Man-Made Fibres"**, by *D.E. Morris (Belgium),* and
- **"Development Tendencies in Fibres and Fibrous Materials: Vision of New Technologies and Creation of New Fibre Generations in the 21st Century"**, by *K.E. Perepelkin (Russia)*.

All the remaining presentations were grouped into the following seven blocks:

- Main problems of developing textiles and fibrous composites
- Chemical fibres formation. New fibres.
- Textile technology
- Finishing and dyeing
- Technical and speciality textiles
- Fibrous composites
- Material science: structure, properties and quality control of fibres and textiles

The first block included presentations which focus on important directions in 21st-century research into fibres & textiles.

As an example, some of them are listed below:

- **'Current Trends in Textile Research'**, *H. Planck, E. Singer (Germany).*
- **'Method of Automatic Design of Woven Fabric Definite Constitution Technology'**, *S.D. Nikolaev (Russia).*
- **'Modern State and the Future of Research & Development and Production of Bioactive Fibres for Medical Application'**, *V.A. Zhukovski (Russia).*
- **'Aspects of the Developments of Special Types of Polypropylene Fibres'**, *D. Budzak, M. Jambrich, J. Kochan, M. Revus (Slovakia).*
- **'Production of Cellulose Composites: Present-Day Physical-and-Chemical Issues'**, *L. Akim (Russia).*
- **'Evolutionary Algorithms in Optimal Design of Composite Structures'**, *A. Muc, W. Muc (Poland).*

This was the first time that a conference on present-day fibres and fibrous materials had been organised in Russia, and was accompanied by an exhibition of presentations from different companies and their achievements, and elaborations from universities related to the conference topics. Some interesting discussions between specialists of different countries took place during the Conference. The Conference National Committee also organised some excursions for the conference guests in the city and the surroundings of Saint Petersburg.

The organisers' intention, based on the opinion of participants and speakers, is to organise the next Conference 'Fibrous Materials – 21st century' of a similar character in May 2007, also in Saint Petersburg, Russia, by the Saint. Petersburg State University of Technology and Design.

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