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Structure of polypropylene/polycarbonate blends crystallized under pressure*

Dominik Paukszta, Józef Garbarczyk† and Tomasz Sterzyński
Faculty of Chemical Technology, Poznań University of Technology, Pl. Sklodowskiej-Curie 1, PL-60-965 Poznań, Poland
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An analysis has been carried out of the crystalline structure of a blend consisting of amorphous polycarbonate and semicrystalline isotactic polypropylene (PP) crystallized under pressure. Structure investigations were carried out by means of wide-angle X-ray scattering. The amount of particular phases as well as the degree of crystallinity have been analysed. It was found that during pressure crystallization, as well as the monoclinic α-modification, the triclinic γ-form of PP also occurs, which disappears after recrystallization in non-pressure conditions. The crystallinity of PP in the blends is independent of the composition of the polymeric mixture.

(Keywords: blends; isotactic polypropylene; polycarbonate)

Introduction

Although the structure of most polymers forming blends is known, the problems of interactions between components during crystallization and the supermolecular structure of the final product still remain unsolved[1].

The structure of blends is connected with compatibility and miscibility of components determined by their molecular structure, and depends on thermodynamic conditions of mixing as well as on actions of external forces, such as electric field or pressure, during crystallization.

In our earlier work we examined blends composed of semicrystalline poly(ethylene oxide) (PEO) and amorphous poly(methyl methacrylate) crystallized in the presence of a strong electric field[2]. Electrocrystallization of those blends caused a significant increase in the nucleating density of PEO samples. We have also found a negative influence of electric field on the formation of β-modification in isotactic polypropylene doped by β-nucleants[3].

The influence of pressure on the structure of pure and doped isotactic polypropylene has been the subject of many investigations, which have shown a significant influence of pressure on polymorphism[4–7].

This work continues our studies undertaken to explain some phenomena occurring during crystallization of melted polymeric blends in an electric field and under pressure.

The aim of the present work is to analyse the crystalline structure of a blend consisting of amorphous polycarbonate (PC) and semicrystalline isotactic polypropylene (PP) crystallized under pressure.

The mechanical behaviour and morphology of PP/PC blends obtained in an internal mixing chamber and also in a twin-screw extruder have been examined by Favis and co-workers[8–10]. The morphology of the samples, with different compositions and obtained with various processing parameters, was estimated on the basis of optical and electron microscopy. The authors found that the size and shape of PC particles dispersed in PP matrix depend significantly on processing conditions as well as on the contribution of particular components.

Experimental

Materials. High molecular weight semicrystalline isotactic PP (VB 65, produced by Neste Oy) and amorphous bisphenol-A PC (Makrolon 2800, produced by Bayer AG) were used in our experiments. Samples of pure polymers and PP/PC blends containing 10 wt% PC (PP10PC), 20 wt% PC (PP20PC), 30 wt% PC (PP30PC), 40 wt% PC (PP40PC), 50 wt% PC (PP50PC), 60 wt% PC (PP60PC), 70 wt% PC (PP70PC), 80 wt% PC (PP80PC) and 90 wt% PC (PP90PC) were investigated.

Sample preparation. The binary blends were prepared by extrusion using a single-screw extruder (Fairex) with screw diameter 30 mm and screw ratio $l/d=25$. The rotation speed was 30 rev min^{-1} and the barrel temperatures were 483, 513, 523 and 533 K. A cylindrical extrusion die, with diameter 3 mm and length 25 mm, was applied. The extruded rods were cooled in a water bath and pelletized.

Crystallization under pressure. Blends and particular components were crystallized under pressure in a special casting mould placed in a hydraulic press. The samples were heated up to 533 K, kept at this temperature for 15 min and subsequently cooled slowly under pressure down to room temperature. The applied pressure was 30 MPa and was kept constant during crystallization. The temperature and pressure programme of sample preparation is shown in *Figure 1*. High homogeneity of temperature and pressure distribution during crystallization permits samples with high isotropy to be obtained.

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† To whom correspondence should be addressed

Structure investigations. Structure investigations were carried out by means of wide-angle X-ray scattering (WAXS), using CuKα radiation ($\lambda = 1.5418$ Å). The measurement conditions were 30 kV and 25 mA. The resolution of multipeaks was performed by a method proposed by Hindeleh and Johnson[11,12], improved and programmed by Rabiej[13]. On the basis of separated diffraction lines (*Figure 2*), the amount of particular phases as well as the degree of crystallinity were analysed. In our system we suppose that there are four structural phases: amorphous PP, amorphous PC, and two crystalline forms of PP, the α-form and the γ-form.

Results and discussion

The WAXS patterns of selected samples are presented in *Figure 3*. *Figure 3a* shows a diffraction pattern for the pure isotactic PP and *Figure 3b* for the amorphous PC. *Figures 3c* to *3f* present WAXS patterns for PP/PC blends with various PC contents.

For the PP sample, only the most stable monoclinic α-form is seen (*Figure 3a*). However, in a sample containing 10 wt% PC (*Figure 3c*), a significant reflex at 10.0° appears, indicating the presence of triclinic[6,14] or orthorhombic[15,16] γ-phase. In the case of the triclinic form, this reflex has (1$\bar{2}$0) index; however, in the orthorhombic form, where Meille *et al.*[16] proposed a non-parallel arrangement of polymer chains, the reflex in question is indexed as (117).

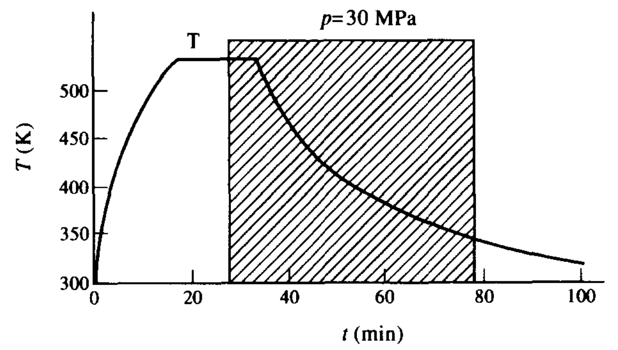

Figure 1 Temperature and pressure (shaded area) programme applied during preparation of the samples

The other reflexes, originating from both polymorphic modifications, overlap and therefore the presence of the phases in question can be detected on the basis of observation of two independent reflexes at 10° (1$\bar{2}$0) (γ) and at 9.30° (130) (α).

In the diffraction pattern of samples containing more than 10 wt% PC, the γ-form PP, as well as the α-form, was still observed; however, when contents of PC exceed 60 wt%, the WAXS patterns look less clear (*Figure 3f*). Therefore, results presented here concern only blends containing not less than 40 wt% PP.

The changes in amount of γ-phase were determined as a ratio of the area under diffraction lines originating from the γ-form ($F\gamma$) to the area originating from both phases ($F\gamma + F\alpha$). As seen in *Figure 4*, the amount of the γ-phase oscillated between 30 and 40% and showed growth of a few per cent.

According to the literature, the γ-phase of isotactic PP can be formed by crystallization of high molecular weight polymer under high pressure (386 MPa)[4], during crystallization without pressure[17], or under medium pressure (~20 MPa)[5] of low molecular weight fractions. This form may also be obtained by melt crystallization starting from a fraction of a random ethylene–propene copolymer soluble in *p*-xylene[6].

The pressure used in our experiments was much lower than that applied by Sauer and Pae[4]. On the other hand, the lack of γ-form PP in blends crystallized without pressure showed that the presence of PC cannot be considered as the only reason for formation of this modification. The above observations proved that only the coexistence of elevated pressure and the presence of PC cause formation of the γ-form PP as well as the α-modification.

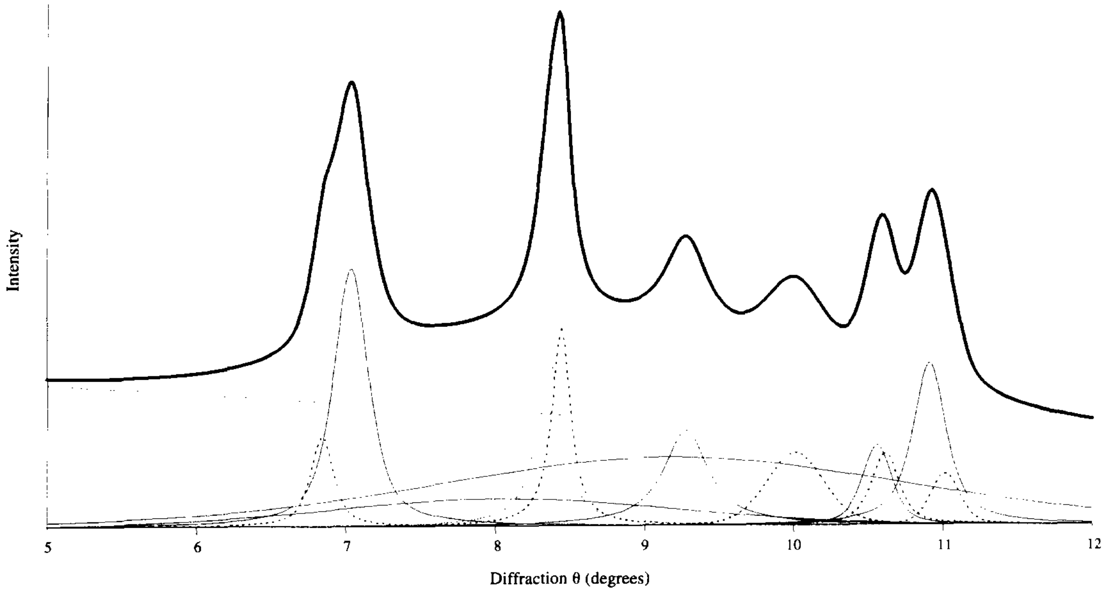

Figure 2 Method of separated diffraction lines. The top curve presents the experimental diffraction pattern. The dotted curves concern the γ-phase of PP and the continuous curves concern the α-phase of PP

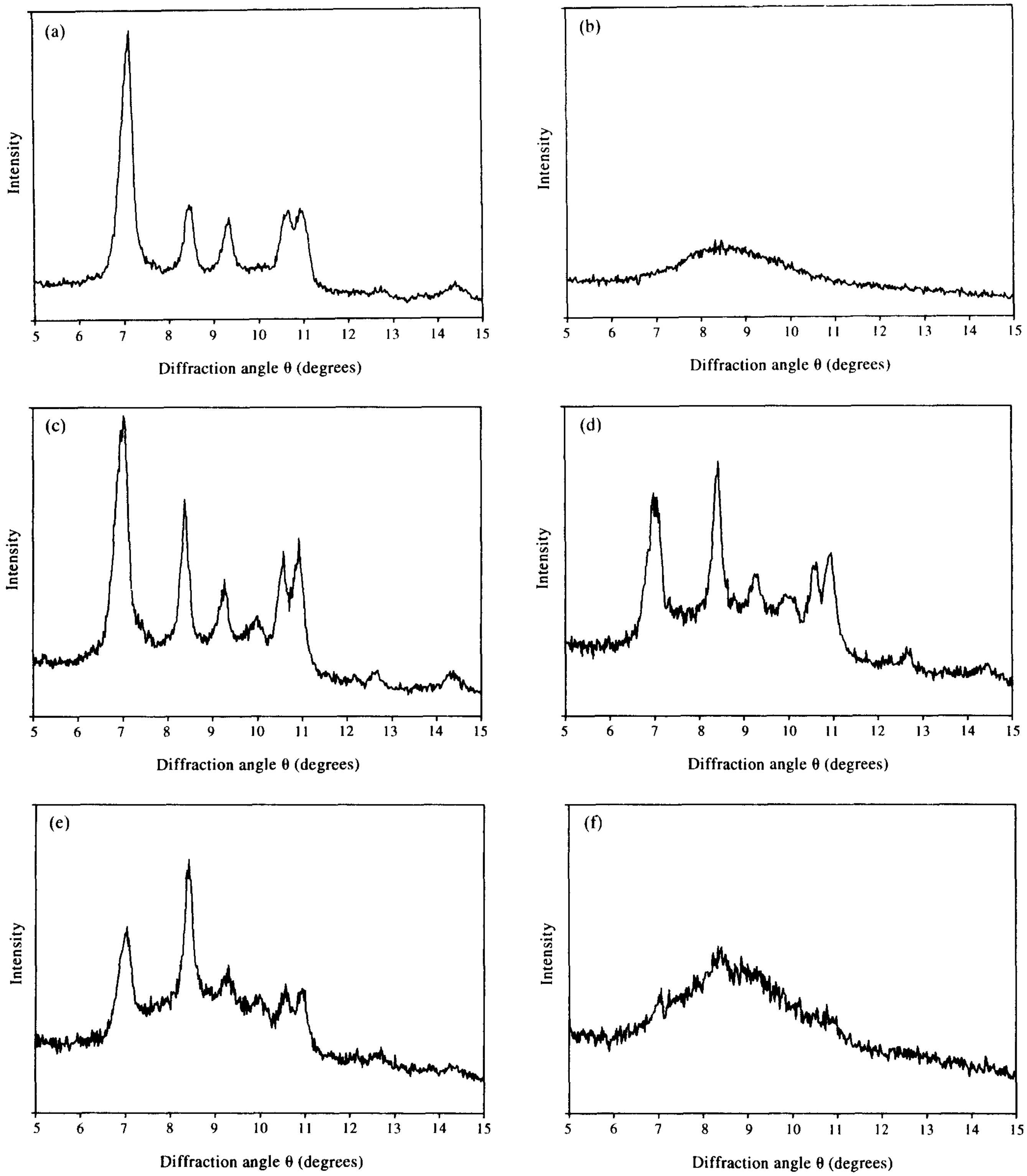

Figure 3 Wide-angle X-ray scattering patterns of samples of (a) PP; (b) PC; and the following PP/PC blends: (c) PP10PC; (d) PP40PC; (e) PP60PC; (f) PP90PC

The absence of γ-form PP in PP (*Figure 3*), as well as in PP/PC blends crystallized without pressure (*Figure 5*), does not explain the phenomenon by epitaxial growth of γ-form on the surface of α-lamellae, which was particularly considered by Lotz *et al.*[18]. Neither can it be explained by epitaxial growth of γ-form PP on the surface of solidified PC. According to the suggestion given by Meille *et al.*[16], an essential reason for formation of the γ-phase lies in the thermodynamic conditions of crystallization of PP.

We cannot exclude additional effects of physico-mechanical interactions between PP and PC, because both components characterize various specific volume properties as a function of temperature. Analogous interactions in polyethylene/PP blends were suggested by Leclair and Favis[19].

The γ-form obtained in our experiment is unstable, because it disappeared after melting and recrystallization without pressure (*Figure 5*).

On the basis of separated reflexes and amorphous

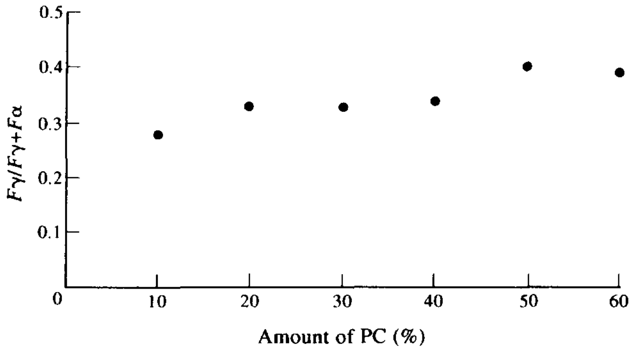

Figure 4 Changes in the amount of the γ-form *versus* the amount of PC in the blends

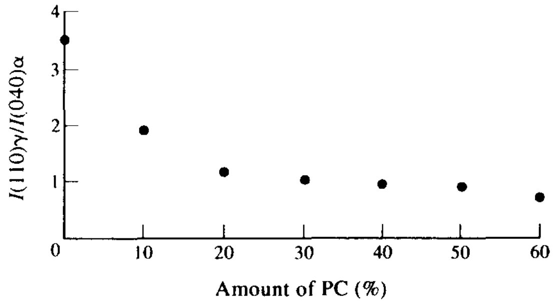

Figure 6 Ratio of intensities $I(110)\alpha/I(040)\alpha$ *versus* composition of the blend

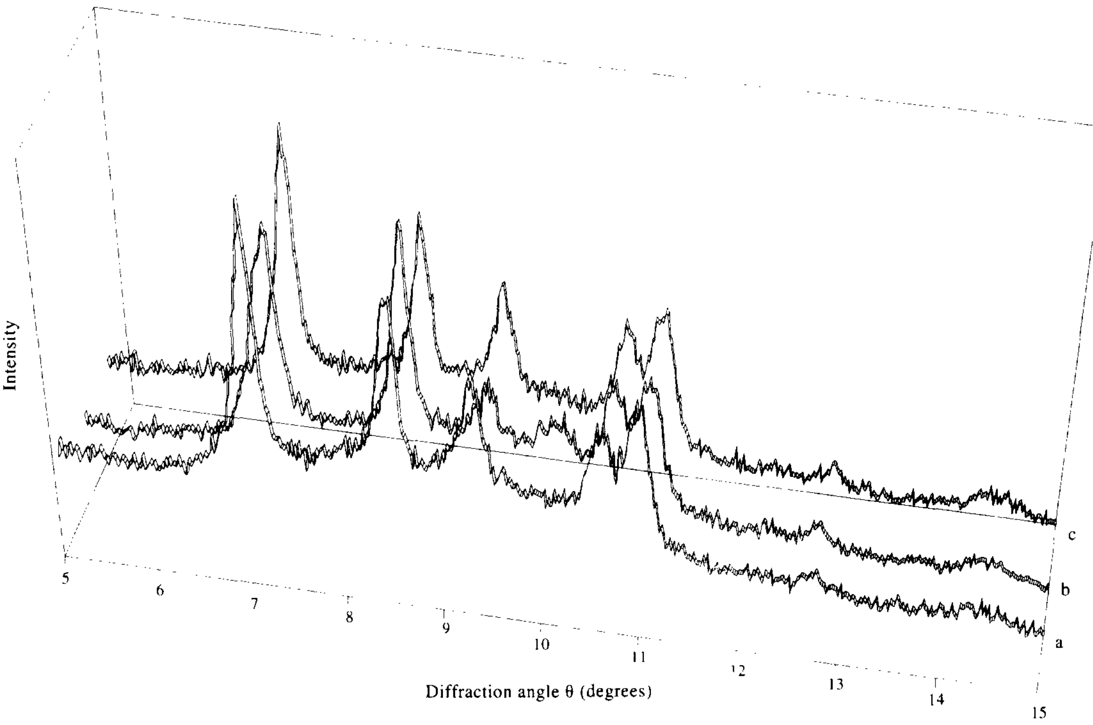

Figure 5 X-ray diffraction patterns of PP30PC: (a) starting sample crystallized without pressure; (b) sample crystallized under pressure; (c) sample subsequently melted and recrystallized in non-pressure conditions

background for both polymers, the degree of crystallinity of isotactic PP was determined. It was interesting that the crystallinity of isotactic PP remains practically unchanged (in the range of 60–70%) in spite of the increase in the content of non-crystalline PC.

Analysis of the intensity of particular separated peaks indicated a decrease in intensity of the peak at 7.07° and a simultaneous increase in intensity of the reflex at 8.30° (*Figure 6*).

The positions of these peaks suggest that in both forms anisotropic structural changes take place. However, our other experiments[7] with PP crystallized under slightly elevated pressure (0.25 MPa) suggest that such changes are connected with the α-form only.

Conclusions

During pressure crystallization of isotactic polypropylene/polycarbonate blends, besides the monoclinic α-modification, the triclinic γ-form of polypropylene also occurs. This form is absent after crystallization of the polypropylene at the same thermal and pressure conditions.

Crystallinity of polypropylene in polypropylene/polycarbonate blends remains at the same level, independent of the composition of the polymeric mixture.

The obtained γ-phase of polypropylene disappears after recrystallization in non-pressure conditions.

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