

The Properties of Polyolefins Modified with PET Powder

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ABSTRACT: The polyolefin and poly(ethylene terephthalate) (PET) products are the mostly current communal waste materials. The waste polymeric materials are generally difficult to separate, and therefore a processing of non-separated materials presents an interesting alternative suggestion. The aim of our work was to analyze the possibility of reprocessing of polyolefins by a relative low temperature, and to study the effect of addition of PET solid powder on

processing and application properties. The results of our investigations allow to conclude that the solid PET powder may play a role of a heterogeneous nucleator, acting as an α -phase promoter of an isotactic polypropylene. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1993–1999, 2008

Key words: composite; fillers; polyolefins; polyesters; mechanical properties

INTRODUCTION

The permanently increasing quantity of wasted plastic products obliges scientific and industrial environment to look for new reprocessing technological solutions. The essential difficulty is the necessity of segregation of wasted polymers. If industrial scraps are relatively easy to process, because of relatively small contaminants and easy segregation of these materials, the reprocessing of municipal plastic waste is more problematical. Therefore, nowadays the renewal of mixed waste polymers has become an important matter, and this fact allows avoiding inconvenient operation of sorting in reprocessing.

The polyolefins like polyethylene (PE) and polypropylene (PP) as well as poly(ethylene terephthalate) (PET) belong to predominant part of commonly used packing materials. These items are often utilized separately, however the technology of recycling of complex materials, finding bigger and bigger attention today, has included these polymers too,^{1–4} is what concerns most of the commonly used polymers in the packaging field.⁵ The rheological and mechanical properties of blends of PET with PE or/and PP (by a PET content of 20–80 wt %) were investigated by Avila and Darte,⁵ and it was found that the viscosity and the properties of those composites were generally decreasing. As an explanation, an effect of the phase inversion, by increasing content of one of the component, was suggested. The

same authors have investigated the influence of a compatibilizer, and it was ascertained that for the blends of recycled PET/PEHD the most effective compatibilizer was maleic anhydride and EGMA. The addition of both products has improved the dispersion of the minor phase and the mechanical properties of the investigated blends.

In the literature, numerous articles dealing with the heterogeneous nucleation, and its impact on structure and properties of polyolefins may be found.^{6–15} Mostly, well-known additives like talk, natrium benzoate, or/and derivatives of sorbitol are used to improve the processing or/and specific properties of polymeric products. The heterogeneous nucleation in polyolefins is a known way of modifying of several properties where especially the transparency, by use of derivatives of sorbitol and brittle to ductile fracture transition by use of specific β -nucleating agents in isotactic polypropylene (iPP) may be cited. The last effect (α - to β -transition by iPP) is also well visible in characteristic changes of the strain–stress curve, and particularly in lower E -modulus and higher elongation observed in the case of β iPP. Another effect observed as a consequence of the addition of specific nucleating agent is an increase of the crystallization temperature,¹⁵ a significant parameter employed by an improvement of processing of thermoplastic semicrystalline polymers.

The PET content in the waste material, as observed nowadays, is usually in the range between 20 and 80 wt %. Regarding the vast progress in modification of PP, and the increasing use of this polymer in food packaging products, the future role of PET and consequently its content in home waste will surely show a decreasing trend. The other

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reason is the way how the PET powder may be prepared, e.g., by solid state pulverization; a modern technique, but with a very low production capacity. This is why in our experiments the studied PET content was in the range of 1.5 wt %.

In this article, we present the impact of reprocessing of mixtures of PE and PP with PET on its structure and properties, where one of the components (PET) was introduced in a form of powder, and the mixture was processed in the temperature below the PET melting point. Thus, in this case the PET powder may be considered as a solid additive, and therefore its role as a nucleating agent for the polyolefins may be awaited.

The aim of our work was to check the possibility of reprocessing of polyolefins by a relative low temperature, and to elucidate the effect of addition of PET solid powder on specific processing and application properties. Another purpose of presented research was to define the impact of the pulverized PET powder on mechanical properties of films of PE/PP with PET, processed in temperatures above the melting point of polyolefins (PE or PP, respectively), but below the temperature of melting of PET.

EXPERIMENTAL

The samples of polyolefins with PET powder were prepared in a form of pellets and extruded films. The structure investigation and determination of the mechanical properties were realized according to the procedure described later.

Material

An iPP Malen P F401 and low-density polyethylene (LDPE) Malen E GGNX 18D003, produced by PKN Orlen Plock/Poland, were used. Some specific properties of these polymers are listed below:

iPP with MFI (230, 2.16) = 2.4–3.2 g/10 min, melting point 172.8°C, and crystallization temperature 114.6°C.

LDPE was characterized by density (23°C) $\rho = 0.921 \text{ g/cm}^3$, MFI (190, 2.16) = 0.3 g/10 min, melting point 118.1°C, and crystallization temperature 99.9°C.

The PET was applied in a form of a solid powder, with an average particle size of about 1 μm . The powder was obtained by means of solid state pulverization^{16–19} of a recycled PET.

Sample preparation

The composites of iPP and LDPE with 0.5, 1, and 1.5 wt % PET powders contained in the matrices were studied. The homogenization of iPP and LDPE with the PET powder was assured by means of molten-state extrusion, using a single-screw extruder with a cylinder diameter of 30 mm and the L/D ratio = 24. The pellets of the composites were produced using a cylindrical die with a diameter of 3 mm, and the palletizing unit operating in an extrusion line, after the cooling bath. The processing temperature was higher than melting point of both polyolefins, but lower than melting temperature of PET. Hence, the PET powder was distributed in the polyolefin matrix in a form of solid particles, creating the conditions favorable for nucleation activity of polyolefins.

As the next step a composite film was produced from previously granulated product. In this case an extrusion line consisting of a single-screw extruder (parameters as described earlier), with a flat-slit die with heating system, chill roll device with glossy rotating drum (with a diameter of 0.265 m) along with pulling and rolling system produced by Proma Toruń [Fig. 1(a,b)] was applied. The film was extruded by a slit die with the width of slot equals to 1 mm and the length of slot equals 120 mm. The



Figure 1 Film extrusion line (a), flow out from the flat die and compressed air-cooling of extruded material (b).

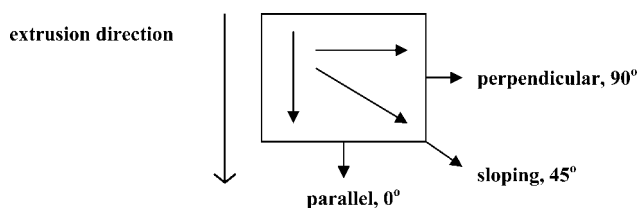


Figure 2 Directions of samples cutting relative to the MD for the mechanical measurements.

extruded material was cooled by air knife directly after the die exit, formed on a chill roll with a hot, metal pull-off roller with a second rubber roller, and finally rolled on a receiving system. On this stage of processing the film may gain an orientation in the longitudinal direction, where the width of the film was slightly reduced. Similarly, as in the primary homogenizing procedure the temperature of film extrusion was kept below the melting point of PET.

The PET powder was produced by means of a solid state pulverization, giving the particles with an average diameter between 1 and 3×10^{-6} m; hence, the PET-filler distribution and the distribution homogeneity in the iPP and PE matrix were determined by means of an optical observation, with satisfactory results.

The adhesion between the PET particles and the iPP matrix is known to be very low, therefore our attention was given to the nucleation role of iPP crystals, played by the PET powder, and not on the fibers reinforcement of the classical polymeric composite materials. It is also known that even if the adhesion of small particles to the polymeric matrix is low, a certain increase of tensile mechanical properties, because of the "debonding" effect, may be awaited. The explanation of this phenomenon may be found in Refs. 20–22 and in our earlier publications.^{23,24}

Method

To verify the influence of solid PET powder on the structure and mechanical properties of LDPE and iPP, the measurements by means of wide-angle X-ray scattering (WAXS), the differential scanning calorimetry (DSC), and mechanical elongation test were realized.

The WAXS experiments were performed by applying a horizontal diffractometer TUR, operating by 20 kV and 30 mA with the $\text{Cu}_{K\alpha}$ radiation giving X-ray beam length $\lambda = 1.5418$ Å. The type of the crystal structure and the structure parameters (position of the WAXS maxima) were analyzed.

The DSC measurements were realized using Netzsch DSC 2000 apparatus. A double melting and crystallization procedure, in the temperature range

from 40 to 200°C (PP/PET), and from 40 to 180°C (PE/PET) was used, where a heating rate of 10°C/min, and a cooling rate of 5°C/min were applied. Melting and crystallization temperature and the corresponding melting enthalpy, characteristic for those polymers were analyzed.

The samples employed for the characterization of the mechanical properties were cut out from the film with the aid of special cutting tool, in a form of dumbbell in the machining direction (MD) (foreseen orientation), perpendicular (TD) to the extrusion flow and placed at an angle 45° to the MD (Fig. 2).

An universal testing machine TIRA test 2200 coupled with computer, with a tensile strength measurement head 0–100 N, was applied for the mechanical tests. The tensile rate was 10 mm/min, and for all type-matters of film the tests were repeated three times in all three directions.

RESULTS

Crystal structure of the composites

For the composites of LDPE with the PET-powder any modification of the PE structure, related to the addition of a low content of the PET powder, was noted (Fig. 3). The unchangeable position of the diffraction peak, independent on the PET-powder content, signifies that in the case of these modification no changes on the elementary unit level nor of the interplanar distance was noted. Because of its highly tactic and regular molecular structure and very low-glass transition temperature, PE prevails a very high-intrinsic crystallization rate.^{25–27} This is the reason of a high-crystal structure stability, where the changes of the elementary unit may be observed only if specific fields are applied during crystallization,^{28–30} as it was the case of electric field-controlled crystallization from the melt. Apparently, the addi-

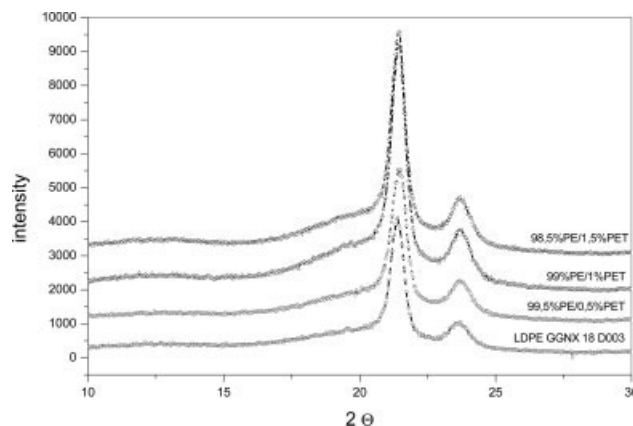


Figure 3 WAXS diffractograms of the PE + PET composites.

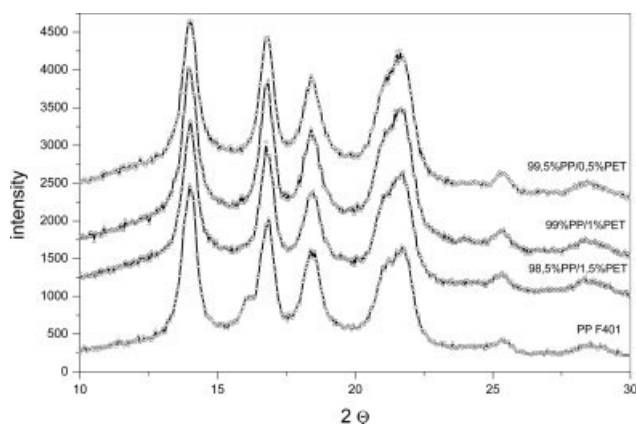


Figure 4 WAXS diffractograms of the iPP + PET composites.

tion of PET powder did not provoke any similar changes of the crystal structure.

On the contrary, on the WAXS diffractograms recorded for the composites of PP with PET, a slight change of the iPP crystal structure may be observed. Mainly, for the pure iPP sample (Fig. 4) a small maximum by the Bragg angle of about $2\theta = 16.5^\circ$, characteristic for the 300 plane may be seen. This maximum indicating the coexistence of both polymorphic α - and β -phase in iPP^{11,26,31–33} disappeared after the addition of a low content of the PET powder. The creation of the pseudo hexagonal β -phase in iPP is probably due to shearing existing during melt-processing of the samples.^{34–37}

It is known that the polymorph iPP structure modification^{6–9} may be realized by an addition of an even low quantity of specific additives, called nucleating agents. Depending on the nucleation agent used^{10,11} as well monoclinic α , as pseudo hexagonal β -phase may be created in iPP. In our case regarding the WAXS structure analysis, the PET powder may be treated as an α -phase promoter. Similarly, by the heterogeneous nucleation realized with derivatives of sorbitols,^{10–12,15} an exclusion of the process induced β -phase formation, because of slightly faster crystallization of specific nucleated iPP, was observed.

Degree of crystallization by DSC

For the composites of PE with PET powder relative low changes of the DSC determined crystallinity of

PE, in the range between 25 and 29% may be noted, where for pure PE the degree of crystallization was about 27%. More sizeable changes of the degree of crystallinity may be observed for the PP/PET systems. In this case the changes of the degree of crystallization of iPP in the range between 31 and 44% were noted, accordingly always higher value for pure iPP and iPP with highest (1.5 wt %) PET powder content was noted.

Crystallization and melting temperature by DSC

More evident are the changes of the phase-transition temperatures determined by DSC. In all cases, as well for PE as for iPP, during first DSC melting a higher melting temperature was observed, comparing with the second melting (Tables I and II). This observation may suggest a somehow higher structure organization³⁸ attained after melt-processing of the composites, relative to the recrystallization induced by DSC-controlled heating and cooling procedure.

Regarding the addition of PET powder any changes of the crystallization temperature were observed for the PE composites, an effect which may be explained by a very high-crystallization rate of this polymer³⁹ as mentioned earlier.

On the contrary, a slight but marked increase of the crystallization temperature of iPP in composites with 1 and 1.5 wt % containing the PET powder was noted. As it was indicated earlier, the PET solid powder may be an origin of a heterogeneous nucleation of iPP, where the evidence of this effect is usually demonstrated by an increase of the crystallization temperature, creation of a fine spherulitical morphology,^{9,15,40} and sometimes modification of the crystal structure. This is probably the case in our investigation; e.g., the increase of crystallization temperature of iPP, in the presence of solid PET powder, may prove an effect governed by the existence of a heterogeneous nucleation.

Mechanical properties

The force at break and Young's modulus were evaluated from of stress–strain curves for both composites, e.g., for the iPP and LDPE modified with various

TABLE I
Degree of Crystallization (*K*), Melting and Crystallization Temperature (*T*) for the PE + PET Composites

Samples formulation		Crystallization				Melting			
PE%	PET%	<i>T</i> 1 (°C)	<i>K</i> 1 (%)	<i>T</i> 2 (°C)	<i>K</i> 2 (%)	<i>T</i> 1 (°C)	<i>K</i> 1 (%)	<i>T</i> 2 (°C)	<i>K</i> 2 (%)
100	0	99.9	27.21	99.8	27.36	118.1	27.80	116.4	28.66
99.5	0.5	99.9	24.89	99.9	25.02	118.1	25.24	115.3	25.27
99	1	99.8	27.61	99.7	27.40	120.0	30.26	114.8	27.46
98.5	1.5	100.0	29.69	99.7	28.93	117.0	25.45	115.0	24.91

TABLE II
Degree of Crystallization (*K*), Melting and Crystallization Temperature (*T*) for the PP + PET Composites

Samples formulation		Crystallization				Melting			
PP%	PET%	T1 (°C)	K1 (%)	T2 (°C)	K2 (%)	T1 (°C)	K1 (%)	T2 (°C)	K2 (%)
100	0	114.6	44.00	114.5	44.03	172.8	37.63	170.6	43.08
99.5	0.5	114.0	31.32	114.1	31.65	172.9	29.37	169.8	31.32
99	1	115.5	34.85	115.4	33.82	173.0	30.30	170.8	30.80
98.5	1.5	115.9	45.11	115.3	44.65	173.3	39.29	169.3	34.32

concentrations of PET powder. In Figures 5 and 6 the results of mechanical tests performed in three various directions relative to MD (compare Fig. 2), in dependence on the PET powder content, are presented. To define the influence of PET powder on the mechanical properties of the polyolefin matrix, the results of the measurements are presented as comparative values, related always to the corresponding values attained for nonmodified polymeric films.

For the composites of LDPE with PET powder the influence of the draw direction is presented in Figure 5. Considering the influence of machining-induced orientation, we have found an increase of force at break for the samples cut in the MD, higher values of the modulus for samples with all PET concentrations, cut in the direction sloped 45° relative to the MD, and lowest values of *E*-modulus in the TD. This effect signifies a certain orientation of the LDPE film induced by slit die extrusion, followed by drawing in a molten state, using a chill-roll device.

An increase of the force at break was observed specially for the samples cut in the MD, e.g., parallel to the direction of film extrusion. In the case of pure LDPE the value of force at break was 14.7 N, and an increase to a value of about 16.8 N, for the composite containing 1.5 wt % PET, was observed. Similarly, an increase of the Young's modulus was observed for the LDPE samples modified with PET, a certain

lowering of the mechanical properties was observed only for composites of LDPE with 0.5 wt % of PET powder. In general, it may be stated that the addition of nonmelted PET powder leads to a several increase of the mechanical properties, with an exception of film samples with the content of 0.5 wt % of PET powder.

For the composites of iPP with PET powder the influence of the draw direction is presented in Figure 6. As well for the force at break, as for the modulus of elasticity the certain dependence on the dog-bond samples cut direction may be noted. The addition of the nonmelted PET powder induced a slight increase of the force at break, where for the modulus lower changes as a function of the PET powder content, were observed.

In all cases by the addition of the PET powder a certain decrease of the modulus for the 0.5 wt % content of the PET powder, followed by a slight increase of this parameter may be noted. It may indicate an influence of both, film drawing melt-processing and addition of solid PET powder on the preferred orientation of an iPP. To detect the real macromolecular organization of the composites, produced by the extrusion film drawn, additional experiments of the state of orientation are foreseen.

In general, for both composites iPP/PET and PE/PET a certain increase of tensile strength was noted. Though, the origin of this effect is not sufficiently

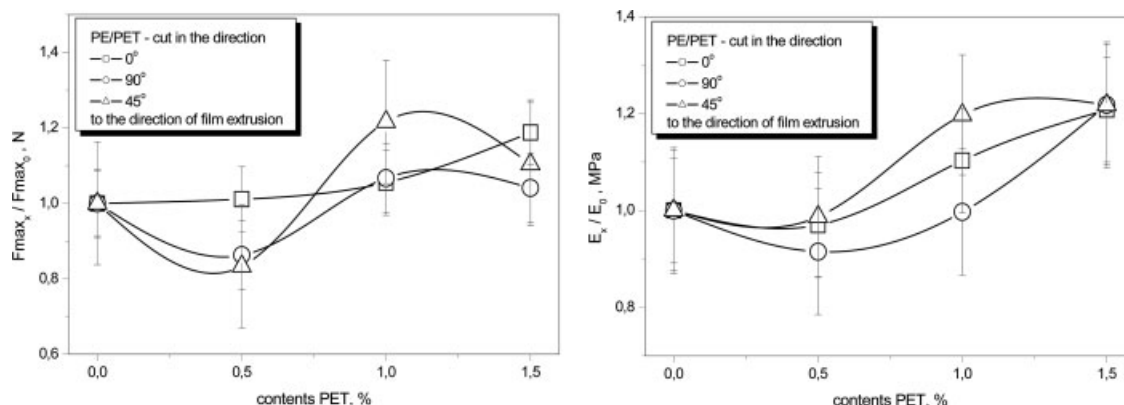


Figure 5 Mechanical properties of films of LDPE with PET as a function of PET content for samples cut in three directions relative to MD.

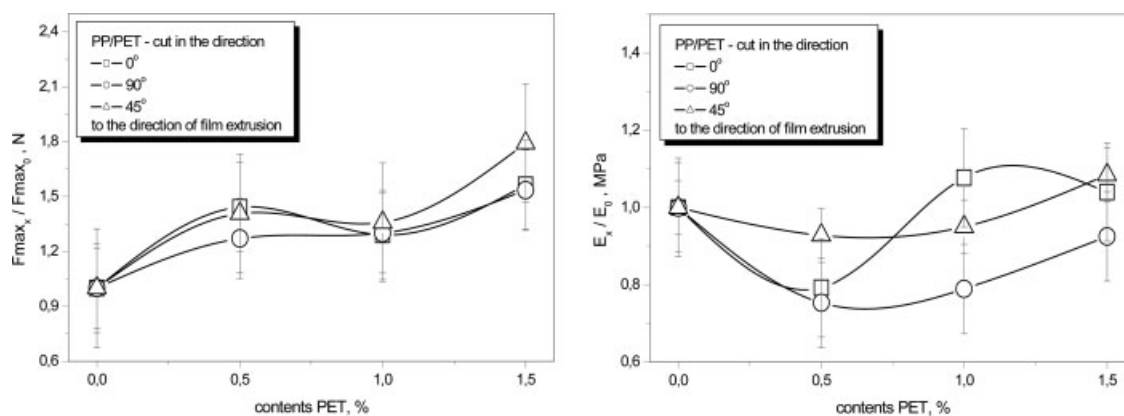


Figure 6 Mechanical properties for films from PP/PET as a function of PET content for all three samples cutting directions relative to MD.

elucidated, a primary explanation based on the “debonding” effect may be proposed. As it was established earlier,^{20–24} in the surrounding area of the particles, during the tensile test a plastic deformation of the matrix may be observed, leading to an increase of mechanical properties. This effect is more pronounced for the measurements performed in the MD (because of flow-induced macromolecular orientation) and for experiments realized with PP as matrix, in comparison with PE/PET composites.

CONCLUSIONS

The structure determination done by means of WAXS as well as the DSC investigations allows to conclude that the addition of PET solid powder in a certain extend leads to a modification of the crystallization of an iPP. This effect may be explained by a possibility of PET powder to play a role similar to a heterogeneous nucleating agent, and acting as an α -phase promoter. This action is somewhat comparable with the known nucleating agents,^{12,15,41} but evidently the nucleation efficiency^{7,8,42} is much lower in this case.

We have shown that the application of powder of waste PET, introduced as filler to commercial polyolefines, is justified from utilitarian point of view, the effect which has an ecological importance. It was observed that the addition of a low amount of pulverized PET does not influence negatively the mechanical properties of produced films, but even leads to an improvement in certain cases.

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