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Effect of electron-beam irradation on pik melting temperature of polymer blends

RAPID COMMUNICATION

Summary — The effects of the electron radiation dose and presence of a compatibilizer on the peak melting temperature (T_{pm}) of the crystalline phase, of granulated polymer blends were studied. The samples were prepared from basic polymer blend composed of low-density polyethylene (PE-LD), high-density polyethylene (PE-HD), polypropylene (PP), polystyrene (PS), and poly(ethylene terephthalate) (PET). As the compatibilizers, the styrene-ethylene/butylene-styrene elastomer grafted with maleic anhydride (SEBS-*g*-MA) or trimethylol propane trimethylacrylate (TMPTA) were used. It was found that addition of compatibilizer irrespective of its type and amount had no significant effect on T_{pm}. Decrease in the T_{pm} value with increase in the electron radiation dose for the crystalline phase of PE-LD, PE-HD, and PP was observed.

Key words: polymer blends, electron-beam irradiation, compatibilizers, peak melting temperature, differential scanning calorimetry.

WPŁYW PROMIENIOWANIA ELEKTRONOWEGO NA TEMPERATURĘ PIKU TOPNIENIA MIESZANKI POLIMEROWEJ

Streszczenie — Zbadano wpływ promieniowania elektronowego i kompatybilizatorów na temperaturę (T_{pm}) piku topnienia fazy krystalicznej granulatu wytłoczonego z mieszanki polimerowej. Próbki wykonano z mieszaniny polietylenu niskiej i wysokiej gęstości (PE-LD, PE-HD), polipropylenu (PP), polistyrenu (PS) i poli(tereftalanu etylenu) (PET). Jako kompatybilizatorów użyto elastomeru styren-etylen/butylen-styren szczepionego bezwodnikiem kwasu maleinowego (SEBS-*g*-MA) lub triakrylanu trimetylolopropanu (TMPTA). Nie zaobserwowano istotnego wpływu rodzaju oraz ilości kompatybilizatora na wartości T_{pm}. Stwierdzono natomiast obniżenie wartości T_{pm} fazy krystalicznej PE-LD i PE-HD, oraz PP spowodowane promieniowaniem elektronowym.

Słowa kluczowe: mieszaniny polimerowe, promieniowanie elektronowe, kompatybilizatory, temperatura piku topnienia, skaningowa kalorymetria różnicowa.

Thermodynamic immiscibility of most polymers is a serious barrier in processing both virgin polymers and plastic wastes. As a consequence, adhesion between individual molecules of the materials made of polymer blends is too low and their mechanical strength is to poor. In order to enhance this strength, small amounts of some chemical substances called compatibilizers are added to the polymer blends. Irradiation of the polymeric material (containing or not containing a compatibilizer) by means of the ionizing radiation, mainly the high-energy electron beam, is another way to enhance the mechanical strength of the material. This radiation may be applied when the manufactured product is composed of only one kind of a polymer or of polymer blends consisting of virgin or reused polymers [1—3]. Some other results of electron radiation such as crosslinking, degradation and surface layer modification of polymers and polymeric materials are described in [4—6].

Improvement in the mechanical properties of the irradiated polymer blends is the main advantage of applying of the elastomeric compatibilizers [7]. A trifunctional monomer trimethylol propane trimethylacrylate (TMPTA) is an effective crosslinking agent, especially for PE-LD, PE-HD, and PP or their blends, when irradiated [8, 9].

The peak melting temperature (T_{pm}) of the crystalline phase of polymer belongs to a group of important physical quantities that have to be taken into account in the processing of thermoplastic crystalline or semicrystalline materials and their blends with other plastics. Therefore, the knowledge of this quantity is necessary in order to design and/or optimise properly various types of material processing, including the processing of plas-

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tic wastes. The measurements of T_{pm} for various polymer blends are carried out by means of differential scanning calorimetry (DSC). These measurements are described in many papers, dealing with the virgin polymers as well as with plastic wastes [10—12].

In the present paper, there are shown the results of investigation of the effects of the high-energy electron radiation and two compatibilizers on T_{pm}, of granulated polymer blends. The blends differ in the kind of a compatibilizer and absorbed radiation dose. The presented results constitute a part of a broader research work, concerning application of the electron radiation and various compatibilizers in order to improve properties of the composites produced from plastic wastes.

EXPERIMENTAL

Materials

The studied samples were re-extruded blends of:

— low-density polyethylene Malen-E FABS 23-D0022 (PE-LD),

— high-density polyethylene Hostalen ACP 5831 D (PE-HD),

— isotactic polypropylene Malen P F 401 (PP),

— polystyrene Owispol 945 E (PS),

— amorphous poly(ethylene terephthalate) Elpet-A (PET).

The first three polymers were supplied by Basell Orlen Polyolefins (Płock, Poland), fourth by Dwory S.A. (Oświęcim, Poland), and fifth one by Boryszew SA, Elana Branch (Toruń, Poland).

The following compounds were used as compatibilizers for the polymers mentioned above:

— styrene-ethylene/butylene-styrene elastomer grafted with maleic anhydride (SEBS-*g*-MA), including 1.7 % of maleic anhydride and 30 % of styrene (Kraton FG 1901X, Shell Chemicals, Houston, USA);

— trimethylol propane trimethylacrylate (TMPTA), a trifunctional monomer (Sigma-Aldrich, Germany).

Preparation of samples

There were studied the samples prepared from basic polymer blend, composed of 24 % of PE-LD, 23 % of PE-HD, 21 % of PP, 15 % of PS and 17 % of PET with the compatibilizers SEBS-*g*-MA or TMPTA added. The samples compositions were reflected in the samples symbols according to the Table 1.

Granulated polymers and compatibilizers were combined at appropriate proportions and initially mixed using a laboratory drum mixer. Then, granulated polymer blends were obtained with use of an extruder. Such a way of the samples preparation, including an additional operation of extrusion, reflects the basic mechanical and heat load, occurring during reprocessing of plastic wastes. Therefore, the results of investigation of such samples may be used to estimate the properties of similar composite materials, produced from these wastes.

Table 1. The kind and amount of compatibilizer used to prepare the samples investigated; the percentages of compatibilizers are specified in relations to the total mass of all polymers in a blend

Symbol of sample	Amount of compatibilizer, wt. %	
	SEBS-*g*-MA	TMPTA
C	0	0
K1	5	0
K2	10	0
K3	15	0
T1	0	1
T2	0	2
T3	0	3

Irradiation process

Irradiation of the granulated samples, with the doses of 25, 50, 100, and 300 kGy, was carried out at the Institute of Nuclear Chemistry and Technology in Warsaw (Poland) using an UELW-101-10 accelerator (NPO TORYJ, Russia).

Method of testing

The melting process was studied by differential scanning calorimetry using a DSC 822^e/700 instrument (Mettler-Toledo, Switzerland).

The DSC measurements were carried out at the ambient atmosphere, according to the procedure specified in appropriate standards [13, 14]. The measuring temperatures were in the range of 20—280 ^{o}C, heating rate 10 deg/min, and sample mass 7—10 g. The value of T_{pm} was determined for PE (PE-LD and PE-HD combined), PP, and PET using a STAR 8 software, supplied by the manufacturer of the DSC 822^e/700 instrument.

RESULTS AND DISCUSSION

Temperatures of the phase transitions for individual polymers, as obtained from the crystalline melting curves recorded by DSC are commonly known which helps to identify the specified polymers. In case of polymer blends, the situation is much more complex: the peaks corresponding to the phase transitions of individual components of the blends may shift and overlap each other. The larger the number of components, the more difficult (sometimes even impossible) identification of individual phase transitions.

The DSC curve with three peaks for the sample C is shown in Fig. 1. The first peak with the maximum at T_{pm1} = 129.45 ^{o}C is wide and clearly asymmetric. It is associated with the melting of the crystalline phases of PE-LD (T_m = 117 ^{o}C) and PE-HD (T_m = 136 ^{o}C) and its

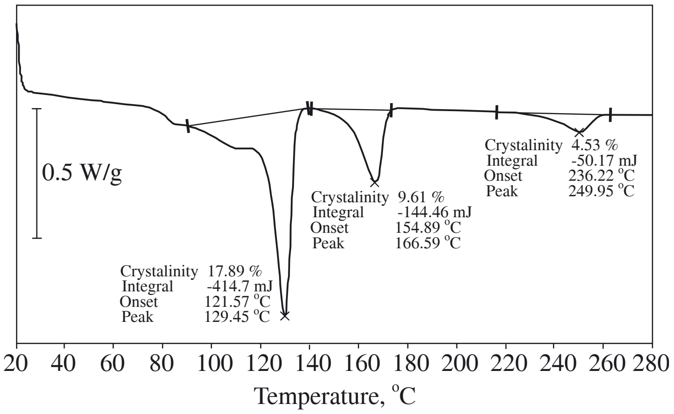

Fig. 1. DCS curve of granulated blend C recorded in the temperature range of 20—280 °C

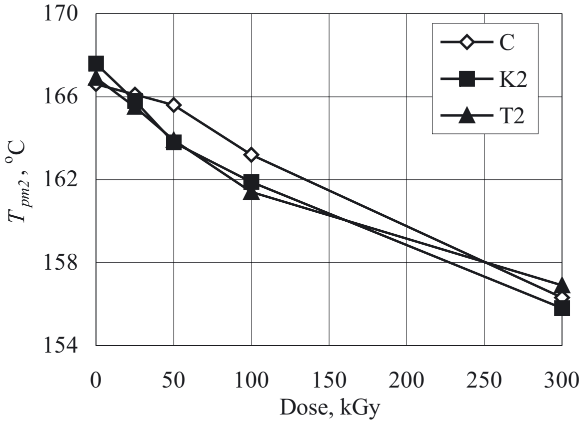

Fig. 3. Effect of radiation dose on the peak melting temperature (T_{pm2}) of the crystalline phase of polypropylene contained in the granulated blends of C, K2, and T2

asymmetry results from the difference in the melting points of these phases. The second peak with the maximum at T_{pm2} = 166.59 °C corresponds to the melting of the crystalline phase of PP. The remaining peak, with the maximum at T_{pm3} = 249.95 °C, is associated with the melting of the crystalline phase of PET.

The DSC curves for both non-irradiated and irradiated samples containing the compatibilizers (K1, K2, K3, T1, T2, and T3) are similar in the shape to those for the samples containing no compatibilizers. Therefore, they are not shown here. The curves for the non-irradiated samples and those irradiated with various doses differ mainly in the positions of T_{pm1} and T_{pm2} while the positions of T_{pm3} do not vary significantly. The latter maxima are contained in the range of 249 °C < T_{pm3} < 252 °C. The observed small variations in the values of T_{pm3} may result from heterogeneity of the materials composed of immiscible components.

A detailed analysis of the influence of the radiation dose on the values of T_{pm1} and T_{pm2} was performed for the samples of C, K2, and T2 *i.e.*, the samples with no compatibilizers and those with medium amounts of these compounds (10 % of SEBS-*g*-MA or 2 % of TMPTA). The results are shown in Figs. 2 and 3. To ease the comparison of the data, the ranges of the y axes have been made to be the same (16 deg) in both of these diagrams. It was found the applied compatibilizers did not cause noteworthy effects on the values of T_{pm1} nor T_{pm2}. The differences in these temperatures are included in the ranges of 0.5—2.0 °C and 0.6—1.8 °C, respectively. Thus, the variations in the values of T_{pm1} and T_{pm2} seem to be random and one may conclude that they are caused by the material heterogeneity of the studied samples. The results of detailed analysis of the influence of the radiation dose on the values of T_{pm1} and T_{pm2} for the samples of K1, K3, T1 and T3 are not presented here because they are similar to those of K2 and T2.

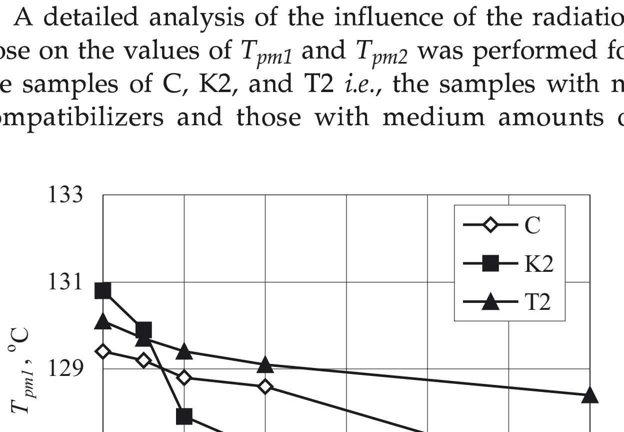

Fig. 2. Effect of radiation dose on the peak melting temperature (T_{pm1}) of the crystalline phase of polyethylene (PE-LD + PE-HD) contained in the granulated blends of C, K2, and T2

As seen in Figs. 2 and 3, the values of T_{pm1} and T_{pm2} decrease with the increasing radiation dose. The changes of T_{pm2} (*i.e.*, ΔT_{pm2}) upon the radiation dose are much larger than of T_{pm1} (*i.e.*, ΔT_{pm1}). Within the entire range of the applied doses (i.e., up to 300 kGy), these changes are in the ranges of 1.7 °C < ΔT_{pm1} < 4.2 °C and 10.0 < ΔT_{pm2} < 11.8 °C).

The observed influence of the radiation dose on the peak melting temperatures of the crystalline phases of PE-LD, PE-HD, and PP, being the components of the studied blends, is associated with the changes occurring in these polymers. Upon the high-energy electron beam various reactions arise in PE-LD, PE-HD, and PP, among them crosslinking and degradation of the polymers being dominant [1]. A decrease in the peak melting temperature may be explained as an effect of the degradation that is much more intense in PP than in PE-LD and PE-HD. Thus, ΔT_{pm2} is much larger than ΔT_{pm1}. The results presented indicate that the changes of T_{pm1} and T_{pm2} for the studied granulated blends are similar to those observed for single polymers, PE-LD or PE-HD [10, 11], and for PP blended with thermoplastic elastomers [15].

The electron radiation insignificantly influences T_{pm3}, which indicates that no distinct changes occur in PET structure. It results from the fact that phenyl groups in PET backbone chains efficiently protect this polymer from the effects of the radiation doses applied (*i.e.*, up to 300 kGy). The results of earlier investigations prove that noticeable changes in the peak melting temperature of the crystalline phase of PET itself occur upon much larger doses of the electron radiation: the dose of 4000 kGy causes the decrease in this temperature only by 4.4 °C and that of 10 000 kGy, by 9.7 °C [16].

CONCLUSIONS

— The increase in the electron radiation dose causes a decrease in the peak melting temperatures of the crystalline phases of PE-LD, PE-HD, and PP that constitute the granulated blends studied. The lowering of the peak melting temperature of the crystalline phase of PP is much larger than that of PE-LD and PE-HD.

— The compatibilizers (SEBS-*g*-MA and TMPTA) affect insignificantly the peak melting temperatures of the crystalline phases of individual polymers that compose the blends.

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