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Study of the change in polarity of polypropylene modified in bulk by polar copolymers

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The adhesive properties of the blends of isotactic polypropylene with ethylene-acrylic acid copolymers were investigated. It was found that the surface free energy, polar component of surface free energy, polar fraction and mechanical work of adhesion increased with concentration of EAA copolymers in the iPP blends to a degree exceeding additive function. The proportionality of mechanical work of adhesion of the polymer blends to polar fraction that reflects the strength of adhesive joint was also revealed. This observation permits us to claim that the increase in polarity or hydrophilicity of iPP due to modification in bulk by the use of polar EAA copolymer raises the strength of adhesive joints between iPP and more polar polymers. The relationship between mechanical properties of the studied polymer blends and their composition showed the functional additivity of the mechanical parameters.

1. Introduction

Isotactic polypropylene (iPP) is one of the most widely used polymers. As iPP is frequently employed in packaging industry its efficient gluing and uncomplicated printing ink application are a matter of necessity. Owing to insufficient surface and adhesion efficiency, especially low surface free energy (SFE, ca 30 $\text{mJ} \cdot \text{m}^{-2}$), this postulate is not fulfilled and in general, the adhesion of iPP is very low because the formation of strong adhesive joint cannot come into being in the absence of polar functional groups in polymer. For obtaining plausible value of adhesion it is necessary to introduce some polar groups into the surface of iPP by using a convenient modification method. Different modification procedures have been used for hydrophilization of iPP surface, e.g. oxidation of surface by means of oxidizing agents, flame, UV radiation or plasma of electric discharge [1]. One of the most frequently used modification methods is the modification of iPP in bulk by addition of some more polar statistical copolymers [2–6]. As for the selection of polymer additives must be taken into consideration the miscibility of iPP matrix with copolymer additive [4, 7–9]. The diblock random copolymers contain blocks which are miscible with homopolymer blocks. Ethylenevinyl acetate (EVA) copolymer or ethylene-acrylic acid (EAA) copolymer which form thermodynamically heterogeneous system with iPP and show uniformly dispersed particles can be used as modifier. The increase in adhesive properties of iPP due to addition of polymer modifier is based on the mechanism suggestive of modification mechanism by low-molecular plastifiers [5]. The diffusion of polymer modifier to iPP surface plays the fundamental role as regards the increase in iPP adhesion [10–12].

It has been theoretically analyzed that the diblock EVA and EAA copolymers used as modifiers can improve adhesion between two incompatible polymer and moreover, can raise SFE of the blends of iPP + EVA copolymer or iPP + EAA copolymer if the concentration of modifier in the blend increases. While EVA is statistically random copolymer, EAA is a random copolymer in which acrylic acid forms longer blocks in the chain of copolymer. The acid units of EAA copolymer are able to form intermolecular and intramolecular hydrogen bonds that affect origination of transcrystalline region in copolymer and adhesive properties of polymer. The existence of excess surface energy was observed in the blends of iPP with some polar copolymers. After iPP modification achieved by mixing with EAA copolymer, the preferential accumulation of the more polar component of the polymer blend at its surface takes place.

This contribution is concerned with investigation of the adhesive properties of the blends of iPP with two sorts of random EAA copolymers containing different amounts of acrylic acid. IPP was modified in bulk by addition of EAA copolymer. Thus strong adhesive linking was formed at the adhesive joint with polyvinyl acetate because of interfacial interactions between functional groups present in EAA copolymer and polar functional groups in polyvinyl acetate. The mechanical properties of iPP with EAA copolymer such as tensile strength at break and elongation at break were also investigated.

2. Experimental

2.1. Used polymers

Isotactic polypropylene Tatren TF – 411, MFI = 10 g/10 min, $\rho_{23^\circ\text{C}} = 0.91$ g/cm^3, $M_w = 2.13 \times 10^5$ g/mol, (Slovnaft, Slovak Republic), ethylene-acrylic acid copolymers EAA 459 containing 8 wt% of acrylic acid, $\rho_{23^\circ\mathrm{C}} = 0.93$ g/cm^3, MFI = 9 g/10 min and 20 EAA with 20 wt% of acrylic acid (Dow Chemical Co.,USA), $\rho_{23^\circ\mathrm{C}} = 0.93$ g/cm^3, $M_\mathrm{w} = 7.68 \times 10^4$ g/mol, MFI = 5.5 g/10 min, polyvinyl acetate (Polysciences, USA), $M_\mathrm{w} = 1.6 \times 10^5$ g/mol, were used as received.

2.2. Preparation of samples

The blends of iPP with EAA copolymer were homogenized in melt by using the completely filled chamber (30 cm^3) of a Plastograph Brabender mixer PLE 331 (Brabender, Germany) at 190°C for 10 minutes, the number of revolutions being 30 per minute. The foils for goniometric and delamination tests were prepared in a laboratory press Fontinje SR-100 (Fontijne, The Netherlands) at the pressure of 700 kPa and temperature of 200°C. The samples destined for measuring mechanical properties were pressed in steel moulds of 1-mm thickness for 2 minutes. The moulds were taken out from press and cooled between metal plates to room temperature. The blades used for mechanical experiments were cut from pressed plates by means of a hand-operated rack press and matrix.

2.3. Measurement of surface properties of polymer

The SFE of polymer was calculated from goniometric measurements of contact angles (θ) carried out with an instrument Contact Angle Meter Amplival Pol (Zeiss, Germany). The drop of testing liquid (volume 3 μl) was put on the surface of polymer by means of a microinjector. The actual measurement of contact angles was performed in a measuring chamber at 22°C and the relation $\theta = f(t)$, where t is the time, was extrapolated to $t = 0$. The dispersion component and polar component of SFE were calculated by the method of least squares [3, 4] from equation:

$$\frac{(1+\cos\theta)\left(\gamma_\mathrm{LV}^\mathrm{d} + \gamma_\mathrm{LV}^\mathrm{p}\right)}{2} = \left(\gamma_\mathrm{LV}^\mathrm{d} \cdot \gamma_\mathrm{s}^\mathrm{d}\right)^{\frac{1}{2}} + \left(\gamma_\mathrm{LV}^\mathrm{p} \cdot \gamma_\mathrm{s}^\mathrm{p}\right)^{\frac{1}{2}} \tag{1}$$

where θ is contact angle (deg), $\gamma_\mathrm{LV}^\mathrm{d}$ and $\gamma_\mathrm{LV}^\mathrm{p}$ are dispersion component and polar component of SFE of testing liquid (mJ $\cdot$ m^{-2}) and $\gamma_\mathrm{s}^\mathrm{d}$ and $\gamma_\mathrm{s}^\mathrm{p}$ are dispersion component and polar component of SFE of polymer (mJ $\cdot$ m^{-2}).

The total SFE of polymer γ_s was determined as follow:

$$\gamma_\mathrm{s} = \gamma_\mathrm{s}^\mathrm{p} + \gamma_\mathrm{s}^\mathrm{d} \tag{2}$$

Polar fractions x_s^p was calculated from equation:

$$x_\mathrm{s}^\mathrm{p} = \frac{\gamma_\mathrm{s}^\mathrm{p}}{\gamma_\mathrm{s}^\mathrm{d} + \gamma_\mathrm{s}^\mathrm{p}} \tag{3}$$

2.4. Measurement of mechanical work of adhesion

The mechanical work of adhesion was measured by delamination of adhesive joint at 90° using a delamination wheel which was attached to crosshead of a universal testing machine Instron 4301 (Instron, England). The rate of motion of the crosshead of dynamometer used for experiments was 50 mm $\cdot$ min^{-1}. The adhesive joint was prepared by spreading the solution of polyvinyl acetate in ethyl acetate on technical cotton fabric by means of a coating rule with a slit of 0.12 mm. A foil of modified iPP and technical cotton fabric were impregnated with the solution of polyvinyl acetate. Applying pressure with a rubber cylinder made the adhesive joints. Then the material was dried to constant weight and cut up to strips of 25 × 150 mm. The delamination was performed along the length of adhesive joint. The values of mechanical work of adhesion were calculated according to equation:

$$A_\mathrm{m} = \frac{P}{b} \tag{4}$$

Where P is mean force of delamination (N) and b is width of adhesive joint (m).

2.5. Measurement of mechanical properties

The stress-strain dependence of the samples of polymer blends on their composition was examined on a dynamometer Instron 4301. The measurements were carried out at laboratory temperature. The rate of deformation was 10 mm/min. The distance between jaws of the dynamometer at the start of measurement was equal to 50 mm. The number of test specimens was eight in each series. The dependence of stress on deformation of polymer blends was used for evaluation of tensile strength at break and relative elongation at break of polymer.

3. Results and discussion

The results of measurements of adhesive and mechanical properties obtained for the blends of iPP with EAA copolymers are presented in Figs 1–6.

The values of SFE of polymer blends of iPP with EAA 1 (plot a) and EAA 2 (plot b) are represented in Fig. 1 as a function of the content of EAA copolymer in the blend. According to Fig. 1 the values of

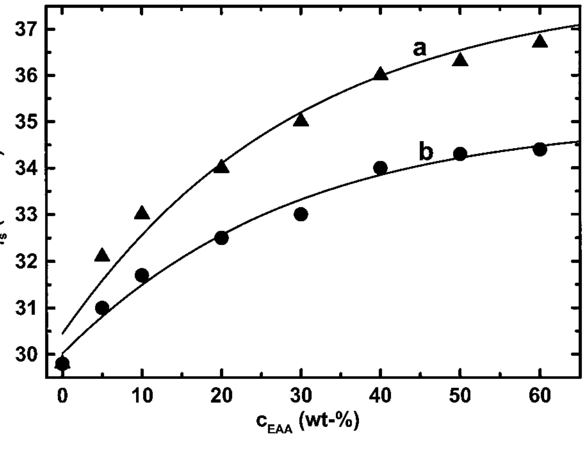

Figure 1 Surface free energy of the iPP modified in bulk by addition of EAA copolymer as a function of modifier concentration: (a) EAA 2, (b) EAA 1.

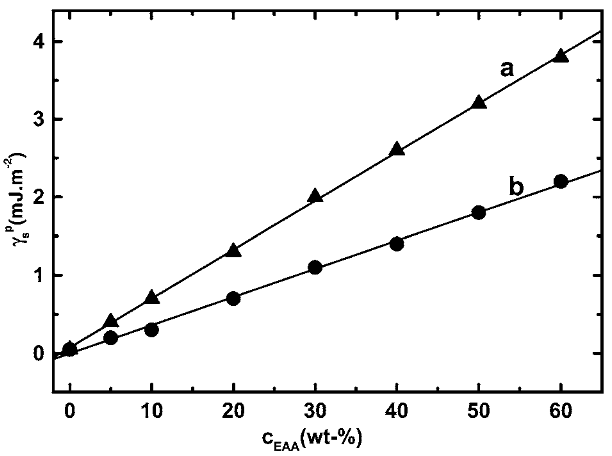

Figure 2 Dependence of polar component of surface free energy of the iPP + EAA copolymer blends on concentration of EAA copolymer: (a) EAA 2, (b) EAA 1.

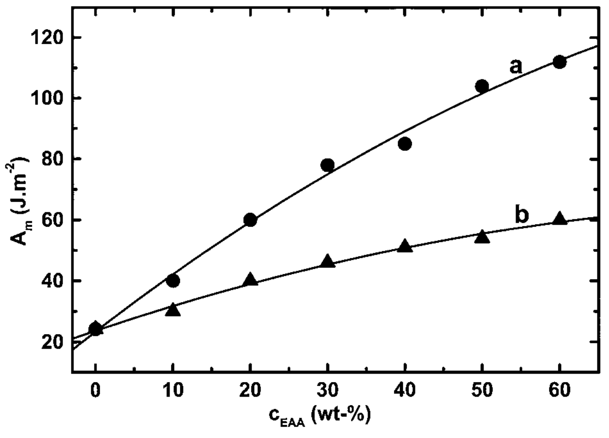

Figure 3 Dependence of mechanical work of adhesion for iPP modified by EAA copolymer to polyvinyl acetate on modifier concentration: (a) EAA 2, (b) EAA 1.

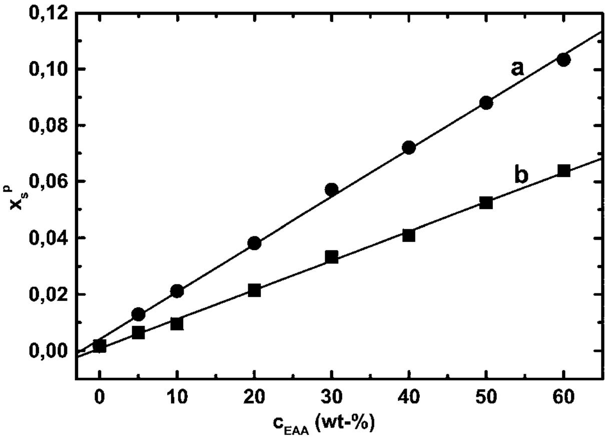

Figure 4 Variation of polar fraction of the iPP + EAA copolymer blends with modifier concentration: (a) EAA 2, (b) EAA 1.

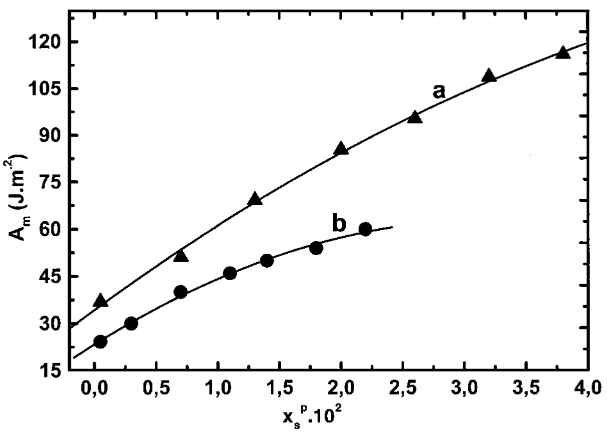

Figure 5 Mechanical work of adhesion for iPP-EAA copolymer blends to polyvinyl acetate as a function of polar fraction: (a) EAA 2, (b) EAA 1.

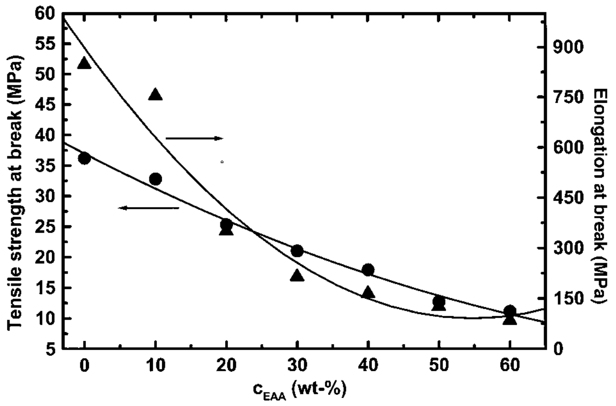

Figure 6 Mechanical properties of the iPP-EAA copolymer blends as a function of modifier content: (a) tensile strength at break, (b) relative elongation at break.

SFE non-linearly increase with concentration of modifier in the blend. The SFE of iPP modified in bulk by addition of EAA exhibited higher value when compared with the values expected on the basis of additivity for the amounts of both polymer components in the blend. The SFE of non-modified iPP is approximately equal to 30 mJ $\cdot$ m^{-2} while the SFE of EAA 1 copolymer (8 wt% of acrylic acid) and EAA 2 copolymer (20 wt% of acrylic acid) are equal to 35 mJ $\cdot$ m^{-2} and 38 mJ $\cdot$ m^{-2}, respectively. It has been found in harmony with the mentioned surface properties of EAA copolymers that the resulting SFE of modifier exhibits higher values for modifier with higher content of acrylic acid. In case iPP was modified by 60 wt% of EAA copolymer, the values of polar component of SFE increased to 34.4 mJ $\cdot$ m^{-2} (for EAA 1) or to 37.4 mJ $\cdot$ m^{-2} (for EAA 2) i.e. expressed in percentage by 15% and 26%, respectively when compared with non-modified iPP.

The different concentration of acrylic acid in EAA (between EAA 1 and EAA 2) corresponding to 12 wt% of acrylic acid brings about a significant increase in polar component of SFE of the blend with iPP. The value of polar component of SFE of iPP in non-modified state approximates to zero. Owing to modification of iPP in bulk the polar component of SFE of modified iPP increased to 2.2 mJ $\cdot$ m^{-2} (EAA 1) or to 3.8 mJ $\cdot$ m^{-2} (EAA 2). The polar components of SFE of modified iPP have linear character and are additive function of polar components of both polymers present in the blend. If we compare the values of SFE with the values of corresponding polar components (Figs 1 and 2) we can state that the non-linear increments in SFE of the blends of iPP with EAA are caused by the increase in dispersion component of SFE of modified iPP accompanying the growing content of EAA in the blend. For 60 wt% of EAA in the blend the dispersion component of SFE increased by 2.4 $\mathrm{mJ \cdot m^{-2}}$ (EAA 1) or 3.1 $\mathrm{mJ \cdot m^{-2}}$ (EAA 2). As the total SFE of the polymer blend is given by the sum of polar component and dispersion component, the total SFE described in Fig. 1 has excess character.

The dependence of the mechanical work of adhesion manifesting itself in delamination of iPP - EAA copolymer blends from polyvinyl acetate on modifier concentration is represented in Fig. 3. In fact, the higher values of mechanical work of adhesion were measured for the modifier with higher concentration of acrylic acid (EAA 2, plot a) than for the modifier with lower concentration of acrylic acid (EAA 2, plot b). The plots in Fig. 3 shows non-linear increase in mechanical work of adhesion while a destruction of adhesive joints with polyvinyl acetate was observed in the range of investigated concentration of EAA copolymer in the blend with iPP. The value of mechanical work of adhesion obtained by delamination of adhesive joints at 90° was 24 $\mathrm{J \cdot m^{-2}}$ for non-modified iPP, 105 $\mathrm{J \cdot m^{-2}}$ for EAA 1 and 165 $\mathrm{J \cdot m^{-2}}$ for EAA 2. The value of mechanical work of adhesion regarding polyvinyl acetate was 60 $\mathrm{J \cdot m^{-2}}$ for iPP modified by 60 wt% of EAA 1 and 112 $\mathrm{J \cdot m^{-2}}$ for iPP containing equal concentration of EAA 2. The significant increase in mechanical work of adhesion regarding polyvinyl acetate obtained by the use of EAA modifiers exceeded the additive function corresponding to relative participation of both components in the investigated blend of polymers.

Determining the contribution of polar component of SFE to its total value can monitor the change in iPP polarity due to modification by EAA copolymer. Fig. 4 represents the dependence of polar fraction for iPP modified by an addition of EAA copolymer on modifier concentration in the blend. According to Fig. 4 we can observe that the polar fraction for the iPP modified in bulk by addition of EAA copolymer increases linearly. Overall, greater increments in polar fraction were measured for blends containing the EAA copolymer with higher concentration of acrylic acid (EAA 2, plot a). The polar fraction found for the iPP modified by EAA 2 copolymer at 60 wt% of modifier in the blend was almost that twofold when compared with the corresponding value obtained for modification by EAA 1 copolymer (plot b in Fig. 4).

Fig. 5 represents the dependence of mechanical work of adhesion on surface polarity of the blend of iPP polymers with EAA copolymers expressed by polar fraction (Fig. 5, plots a and b). According to Fig. 5 the strength of adhesive joint of iPP modified by polyvinyl acetate non-linearly increases with polarity of iPP blends with modifier. The gains in mechanical work of adhesion have been greater for EAA copolymer with higher content of acrylic acid (EAA 2, plot a in Fig. 5) when compared with EAA modifier cntaining lower concentration of acrylic acid (EAA 1, plot b in Fig. 5). The strength of adhesive joints expressed by the values of mechanical work of adhesion in joints for iPP modified by EAA copolymer to polyvinyl acetate can be analyzed by polynomial regression by using a polynomial of second order. Thus the curve a in Fig. 5 gives:

$$A_{\mathrm{m}} = 21.4 + 10.4x_{\mathrm{s}}^{\mathrm{s}} - 0.15\left(x_{\mathrm{s}}^{\mathrm{p}}\right)^2,\ r^2 = 0.99$$

and curve b can be described in the same way, i.e.:

$$A_{\mathrm{m}} = 22.8 + 8.5x_{\mathrm{s}}^{\mathrm{p}} - 0.44\left(x_{\mathrm{s}}^{\mathrm{p}}\right)^2,\ r^2 = 0.99.$$

The high values of correlation coefficients confirm the accuracy of both deduced expressions.

The dependence of tensile strength at break and relative elongation at break of the polymer iPP + EAA blends on content of copolymer is represented in Fig. 6 (plots a and b). According to Fig. 6 the increasing concentration of modifier in the blend containing iPP brings about non-linear decrease in tensile strength (Fig. 1, plot a), i.e. from the value of 37 MPa (non-modified iPP) to the value of 11 MPa for the blend containing 60 wt% of EAA copolymer. Moreover, it was observed that the relative elongation at break (Fig. 1, plot b) decreased from 848% to 85% for the iPP-EAA blends, i.e. by 90% regarding the original value of elongation of non-modified iPP. Both relationships given in Fig. 6 indicate a certain technological compatibility of the investigated polymer components that are thermodynamically incompatible.

4. Conclusions

In conclusion we can state that the adhesive properties of non-polar iPP were significantly influenced by modification in bulk using polar EAA copolymer. The investigations of the iPP + EAA copolymer blends disclosed excess adhesive properties as regards surface energy and mechanical work of adhesion with respect to polyvinyl acetate determined by delamination of adhesive joints. The linear relationships concerning concentration of EAA modifiers corresponding to additive function of both components in the blend were found for polar components of surface energy and polar fractions of the blends. The excess character was confirmed for the dependence of the strength of adhesive joints of iPP modified by EAA copolymers to polyvinyl acetate on polar fraction. The results of measurements confirmed the assumption resulting from preceding experiments with iPP (5) according to which the resulting mechanical work of adhesion regarding more polar polymers can be significantly influenced by polar copolymers. The obtained results are important for achieving higher strength of adhesive joints in the course of iPP gluing as well as for printing ink application to iPP foils during processing of packaging materials. The relationship between mechanical properties of the iPP + EAA copolymer blends and their composition shows the functional additivity of the mechanical parameters, which represent the sum of mechanical properties of both polymer components from their abundance in the blend.

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