Adhesive Behavior of UV Pre-treated Polyolefins

Igor Novák, Ivan Chodák*

Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovak Republic

Summary: The effect of surface modification of polyolefin, mainly isotactic polypropylene and low-density polyethylene, by UV irradiation and phosphoryl chloride on its adhesive behavior was investigated. A non-linear increase of the surface free energy, its polar component and strength of adhesive joint to more polar polymer was observed. The effect of modification of polyolefins was strongly depended on the intensity of the UV radiation. The obtained values of the strength of adhesive joints to polyvinyl acetate correspond with the measured level of hydrophilicity of modified polyolefin.

Introduction

The inferior adhesive properties of polyolefins result in many serious problems especially if gluing or printing on these materials is considered[1–3]. The effective surface modification of polyolefin should lead to a formation of a very thin surface layer with the thickness of several micrometers without affecting the bulk properties of the material. The fine layer of modified polymer on the surface of polyolefin should contain sufficient concentration of the polar moieties leading to an increase of the surface energy of polymer.

Surface modification of polyolefins in vapors of halogen compounds[4-6] under UV irradiation represents an efficient method for the increase of the adhesive properties. The presented method is based on the influence of the UV radiation and vapors of phosphoryl chloride on the polyolefin surface. UV irradiation results in a faster decomposition of the halogene compound and leads to the UV-oxidation of the surface of polymer. Surface modification of polyolefins in vapors of phosphoryl chloride under UV irradiation ($UV/POCl_3$) is a suitable method for the increase of adhesive properties. Phosphoryl chloride behaves as a sensitizer, which decomposes under the effect of UV irradiation. Its decomposition is followed by a formation of

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active chlorine, which takes part in the free radical reactions with polyolefin macromolecules and leads to a formation of -$POCl_2$ groups attached to the polymer chains. At the same time the reaction with oxygen initiated by UV irradiation takes place resulting in a generation of polar oxygen-containing sites.

Experimental

Polymers

The experiment was performed using a commercial polyolefinic products: low-density polyethylene (LDPE) Bralen RA 2 - 19 (Slovnaft, Slovak Republic), a melt flow index (MFI) = 2.0 g/10min, ρ_{22oC} = 917 g/cm^3 and isotactic polypropylene (iPP) Tatren FD 420 containing 0.2 wt-% of UV stabilizer (Slovnaft, Slovak Republic), MFI = 3.2 g/10min, ρ_{22oC} = 905 g/cm^3, polyvinyl acetate, M_w = 1.6 x 10^5 g/mol (Polysciences, USA).

The foils of polyolefins with a thickness of 0.05 mm were prepared by compression moulding at the temperature 170 °C (LDPE) or 200 °C (iPP) in the laboratory press Fontijne SR-100 (Fontijne, The Netherlands) at the pressure 700 kPa.

Chemicals

Ethyl acetate p.a. [Merck, Germany], glycerol, formamide, tricrezyl phopsphate [Serva, Germany], aniline, diethyl phtalate, thiodiglykol, ethylene glycol [Aldrich, USA] methylene iodide [Fluka, Switzerland], benzylalcohol, diethylester of anthranil acid, trichloroethylene [Riedel de Haen, Germany], water was distilled twice before using.

Modification of polyolefins

The PE foils were placed in the glass vessel in the atmosphere of saturated vapors of phosphoryl chloride. The sorption of the UV sensitizer onto the surface of the polyolefin foils took 24 hours. The foils were then irradiated by UV radiation in an open quartz tube having a diameter of 50 mm. The UV light with a wavelength λ = 366 nm was emitted by a 400-W mercury discharge lamp. The distance (d) of the UV tube from the surface of polymer varied between 50 and 200 mm. The relative intensity of UV radiation is inversely proportional to the square ratio of the UV source distances according to the relation:

$$I_r = I / I_0 = (d_0/d)^2 \qquad (1)$$

where I_r is the relative intensity of UV radiation, I_0 (W.s/m^2) is the intensity of UV radiation at the reference distance d_0 = 50 mm and I (W.s/m^2) is the intensity of UV radiation at the distance d (mm).

Measurement of surface properties

The surface free energy and its polar component of polyolefins were measured by goniometric measurements (sessile drop method) using Contact Angle Meter (Zeiss, Germany) with a set of 10 testing liquids. The surface tension of testing liquid was determined by tensometric measurements (tensometer Lauda, Austria). The values of SFE and its polar component were calculated from the contact angles measurement for various testing liquids according to the Fowkes equation[7].

Measurement of the strength of adhesive joint

The strength of adhesive joint to polyvinyl acetate was measured by peeling the adhesive joint. The peel test was carried out using a universal testing machine Instron 4301 (Instron, England) at a crosshead speed 50 mm/min and the length of the adhesive joint 100 mm. Special clamp was used which enables maintaining the 90° angle at joint during the whole test.

Laminates of the polyolefins with polyvinyl acetate were prepared in a laboratory press at a temperature 22 °C under pressure 2 MPa for 1 min. The solution of polyvinyl acetate in ethyl acetate was deposited on the cotton technical fabric (Molino, Slovak Republic) using a coating ruler (Druopta, Czech Republic). The width of the deposited polyvinyl acetate layer was 0.2 mm. The relation for the calculation of strength of adhesive joint measured by peeling is given in the previous paper[7, 8].

Results and discussion

The results of surface and adhesive properties of polyolefins modified by UV/$POCl_3$ are summarized in Figs. 1 - 4.

Fig. 1 shows a non-linear increase of the surface free energy (curve a) and its polar component (curve b) for LDPE as a function of UV modification time in the presence of phosphoryl chloride at the UV source distance of 50 mm.

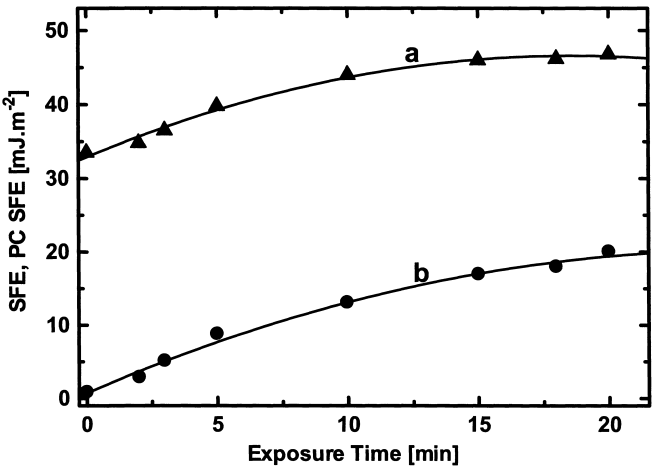

Fig. 1. Variation of the surface free energy and its polar component for LDPE pre-treated by UV/$POCl_3$ with the time of UV exposure (the distance of UV source d_{UV} = 50 mm): a - SFE, b - polar component of SFE.

The surface energy of non-modified LDPE was found to be 33.5 $mJ.m^{-2}$. The surface energy of polymer in the course of modification increased considerably and after 20 minutes gained the value of 46.8 $mJ.m^{-2}$. The polar component of the surface energy for modified LDPE increased strongly from 0.9 $mJ.m^{-2}$ up to 20 $mJ.m^{-2}$. The dependence of the surface energy and its polar component against time levels off after about 10-min period of initial increase. The explanation of this result consists in the saturation of the LDPE surface by the polar oxygen-containing functional groups in the course of modification.

Fig. 2 illustrates a non-linear increase of the surface free energy (curve a) and its polar component (curve b) for iPP modified by UV/$POCl_3$ in the dependence on the time of modification at the UV source distance of 50-mm. The surface energy for non-modified polymer was 30.1 $mJ.m^{-2}$. The surface energy and its polar component of iPP pre-treated by UV/$POCl_3$ increased non-linearly with time up to the value 40.1 $mJ.m^{-2}$ after 20 minutes. This value of the surface energy of modified iPP was considerably lower in comparison with the one obtained for LDPE pre-treated at the same modification conditions.

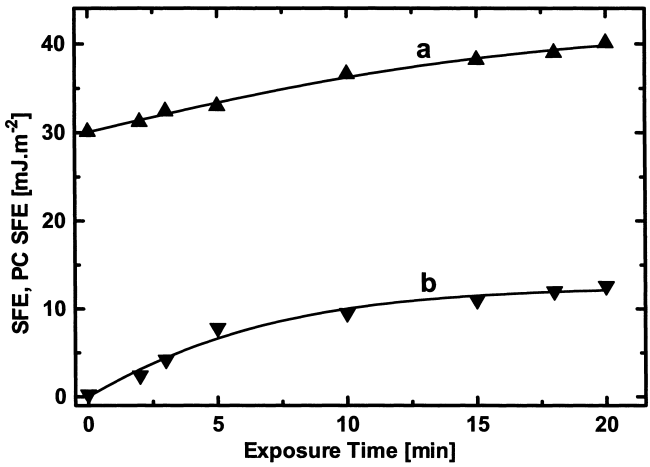

Fig. 2. Variation of the surface free energy and its polar component for isotactic polypropylene pretreated by UV/$POCl_3$ with the time of UV exposure (d = 50 mm): a - SFE, b - polar component of SFE.

The polar component of the surface energy of modified iPP increased after 20 min of modification from 0.25 $mJ.m^{-2}$ up to 12.6 $mJ.m^{-2}$. The time-dependence of the polar component of the surface energy (Fig. 2, curve b) leveled off after an initial increase enduring about 10-min. The explanation of this result is the same as for the modification of LDPE and relates with a surface saturation of polar oxygen moieties of the modified polymer.

The strength of adhesive joints of UV/$POCl_3$ modified polyolefin to polyvinyl acetate measured by 90° peeling is demonstrated in Fig. 3. An UV/$POCl_3$ modification of LDPE leads to the higher value of the mechanical work of adhesion than in the case of iPP adhesive joints[7]. The differences are more pronounced at longer modification time. While the strength of adhesive joints was very low for both investigated unmodified polyolefins, near 26 $J.m^{-2}$, after 20-min of UV/$POCl_3$ modification the substantial increase was observed. The growth of the strength of the adhesive joints was higher for modified LDPE - 204 $J.m^{-2}$ than for modified iPP[7] - 140 $J.m^{-2}$.

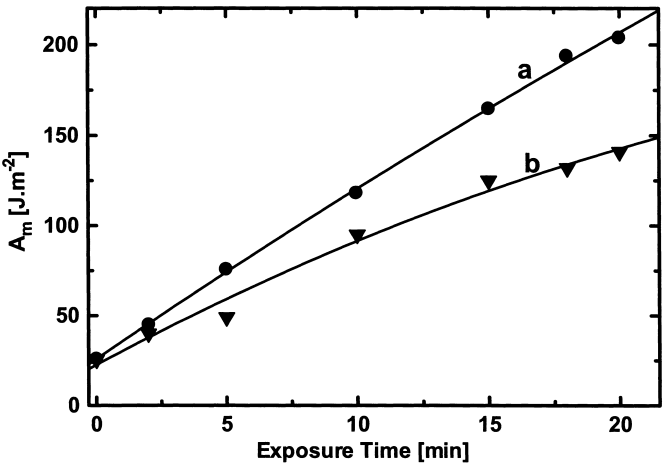

Fig. 3. Variation of the strength of adhesive joint of polyolefin modified by UV/$POCl_3$ to polyvinyl acetate with the time of modification (d_{UV} = 50 mm): a – LDPE, b – iPP.

As expected, the comparison of the Fig. 1 (LDPE) and Fig. 2 (iPP) with the Fig. 3, demonstrates that the strength of adhesive joints of modified polyolefins increases in accordance with the degree of hydrophilicity of modified polymer. Thus, adhesive properties of polymer are strongly related to the values of the polar component of surface energy.

The plot of the polar component of surface energy of modified polyolefins vs the relative intensity of UV radiation is shown in Fig. 4. The intensity of the UV radiation is inversely proportional to the square of the UV source distance from the surface of the polymer. According to Fig. 4, the growth of the UV radiation intensity leads to a considerable increase of the polar component of surface energy of polyolefins. The values of surface characteristics of modified LDPE were significantly higher compared to the modified iPP.

The steep growth of the polar component of surface energy with the increase of relative intensity was observed up to value I_r = 0.25 for both polyolefins corresponding to the distance of the UV radiation source from the surface of polymer.

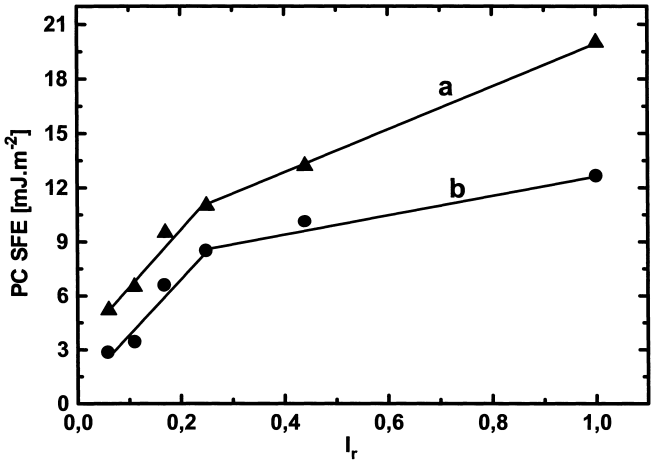

Fig. 4. The polar component of the surface free energy of polyolefin modified by UV/$POCl_3$ (d_{UV} = 50 mm) as a function of the relative intensity of UV radiation: a – LDPE, b – iPP.

Further increase in the relative intensity resulted in less pronounced changes of the investigated surface parameter. This phenomenon can be explained by a summation of factors among whose the mutual deactivation of the radicals formed by UV irradiation at higher radical concentration is supposed to be the most important. The other factors that should be considered, are the decrease of the reaction rate due to diffusion effects and the increase of the surface saturation by polar sites. The increase of the relative intensity of UV radiation of LDPE modified by UV/$POCl_3$ from I_r = 0.06 (the distance of UV source was 200 mm) up to I_r = 1 (the distance was 50 mm) results in a growth of the polar component of surface energy from 5.2 $mJ.m^{-2}$ to the value near 20 $mJ.m^{-2}$, while the change for iPP was from 2.8 $mJ.m^{-2}$ (d = 50 mm) to 12.6 $mJ.m^{-2}$ (d = 200 mm).

Conclusion

The surface energy of polyolefins modified by UV/$POCl_3$ was essentially higher in comparison with non-modified polymer. A non-linear increase of the surface energy and its polar component with time of UV exposure was observed. The pre-treatment of polyolefins by UV/$POCl_3$ method leads to a considerable growth in the surface

and adhesive properties of the polymer, the effect is more pronounced for LDPE in comparison with iPP and it depends on the intensity of the UV radiation as well as on the time of UV exposure. The values of the strength of adhesive joint to polyvinyl acetate of UV/$POCl_3$ modified polyolefin correspond with the measured values of the polar component of surface energy. The efficiency of iPP modification by UV/$POCl_3$ increased substantially by diminishing the distance of UV radiation source from the surface of polymer or by increasing the intensity of UV source.

Acknowledgements

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