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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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Online publication date: 27 February 2001

To cite this Article Novák, I. and Chodák, I.(2001) 'ADHESIVE BEHAVIOR OF UV SENSITIZER MODIFIED LOW-DENSITY POLYETHYLENE', *Journal of Macromolecular Science, Part A*, 38: 1, 11 – 18

To link to this Article: DOI: 10.1081/MA-100000356

URL: <http://dx.doi.org/10.1081/MA-100000356>

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ADHESIVE BEHAVIOR OF UV SENSITIZER MODIFIED LOW-DENSITY POLYETHYLENE

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ABSTRACT

Adhesive behavior of polyethylene modified by UV irradiation and phosphoryl chloride has been investigated. A nonlinear increase of the surface energy and its polar component against time of UV exposure has been observed. The efficiency of polyethylene modification depends strongly on the crystallinity degree of polymer, the intensity of the UV radiation as well as the time of modification. The measured values of the mechanical work of adhesion to polyvinyl acetate correspond with the level of hydrophilicity of the modified polymer. The relation between the mechanical work of adhesion and polar component of the surface free energy has been found.

Key Words: Adhesion; Halogenization; Hydrophilicity; Modification; Polyethylene; Surface Energy; UV Sensitizer

INTRODUCTION

The low hydrophilicity of polyethylene (PE) is caused by its nonpolar macromolecule's structure and, consequently, creates many problems, especially if printing and bonding procedures are applied. Unmodified or unoxidized PE contains no polar groups in the macromolecule. The low surface-free energy (SFE) ($\sim 32 \text{ mJ/m}^2$) and lack of polar groups on the PE surface lead to difficulties in wetting the polymer and in forming strong bond. For the increase of the polarity, various modification

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methods are applied, mainly aimed to an introduction of suitable polar sites into and/or on the chains of polymer (1,2). A number of modification methods have been recently developed and some of them have been successfully used for surface pretreatment of PE, for example, electric discharge plasma at atmospheric pressure (corona discharge) (3), oxidation either by open flame (4) or by chemical methods (5), and the grafting by anhydrides of maleic or itaconic acids (6–8). Considering the methods of PE modification a chemical pretreatment that introduces specific functional groups plays an important role, resulting in strong adhesive bonds. Another mode of modification of PE is based on the removal of weak boundary layer diminishing adhesion and on the creation of surface topography suitable for mechanical interlocking (7).

Among practically important methods used for the increase of PE hydrophilicity, halogenization of polymer seems to be very effective (9–13). The halogenization of PE is based on the influence of gaseous halogens or vapors of halogen compounds on the surface of the polymer. The action of UV radiation leads to a faster decomposition of the modification agent and also to an oxidation of the polymeric surface (5).

The surface modification of PE in vapors of phosphoryl chloride at simultaneous influence of UV irradiation leads to a significant change in surface and adhesive properties of the polymer. Phosphoryl chloride in this case acts as a UV-sensitizing agent. Its decomposition under UV irradiation is accompanied by an evolution of active chlorine. The free radical reaction of the latter with PE macromolecules leads to a formation of $-\text{POCl}_2$ groups attached to the polymer chains (11) accompanied by the oxidation of the polymer during UV irradiation. The polar oxygen-containing sites are created as a product of PE oxidation.

In the article, we have investigated the adhesive and surface properties of PE modified by UV radiation in the presence of phosphoryl chloride. Modification of PE by UV/ POCl_3 results in an increase in surface energy of polymer as well as in an improvement of the mechanical work of adhesion of modified PE to more polar polymers.

EXPERIMENTAL

Polymers

The adhesive properties of commercial grade low-density PE Bralen RA 2-19 (Slovnaft, Slovak Republic) with $\Delta H_{\text{melt}} = 110 \text{ J/g}$ and high-density PE DSM 9089 U (DSM, The Netherlands) with $\Delta H_{\text{melt}} = 216 \text{ J/g}$ have been studied. The PE foils with a thickness of 0.05 mm have been prepared by compression molding at the temperature 170°C (low-density PE) or at 200°C (high-density PE) in the laboratory press Fontijne SR-100 (Fontijne, The Netherlands).



Modification of PE

The samples of PE foils have been placed in a vessel with phosphoryl chloride container. The sorption of the UV sensitizer onto the surface of the polymer proceeded in the saturated vapours during 24 h. After that, the samples were irradiated in air using an open quartz tube (50-mm diameter) by UV light with wavelength 366 nm emitted by a 400-W mercury discharge lamp. The distance of UV tube from polymeric surface varied between 50 and 200 mm. The relative intensity of UV light is inversely proportional to the square ratio of the UV source distances according to the relation:

$$I_{\text{rel}} = I/I_0 = (d_0/d)^2 \quad (1)$$

where I_{rel} is the relative intensity of UV radiation, I_0 ($\text{W} \cdot \text{s}/\text{m}^2$) is the intensity of UV radiation at the reference distance $d_0 = 50$ mm and I ($\text{W} \cdot \text{s}/\text{m}^2$) is the intensity of UV radiation at the distance d (mm).

SFE Measurement

The measurement of the SFE of PE and its polar component was carried out by goniometric measurements using Contact Angle Meter (Zeiss, Germany) with a set of 12 testing liquids. The surface tension of the testing liquids was measured by tensometer (Lauda, Austria). The drops of the testing liquids have been deposited on the surface of the polymer and the contact angle was measured in 30-second intervals for 10 min. The values of SFE and its polar component were calculated from the contact angles values for various testing liquids by least square method according to the Fowkes equation (13,14).

Adhesive Measurement

The mechanical work of adhesion to polyvinyl acetate (Polysciences, USA) was measured by peel test of the adhesive joint at a constant 90° angle. The peel test was performed in a universal testing machine, Instron 4301 (Instron, England) at a crosshead speed of 50 mm/min and the length of the joint was 100 mm.

Laminates of the nonmodified and modified PE with polyvinyl acetate were prepared in a laboratory press at a temperature 22°C under pressure 2 MPa for 1 min. The deposition of polyvinyl acetate solution in ethyl acetate on the cotton technical fabric (Molino, Slovakia) was carried out using a laboratory equipment (Druopta, Czech Republic). The width of the deposited polyvinyl acetate layer was 0.2 mm. The equation for the calculation of mechanical work of adhesion is given in the previous paper (3).



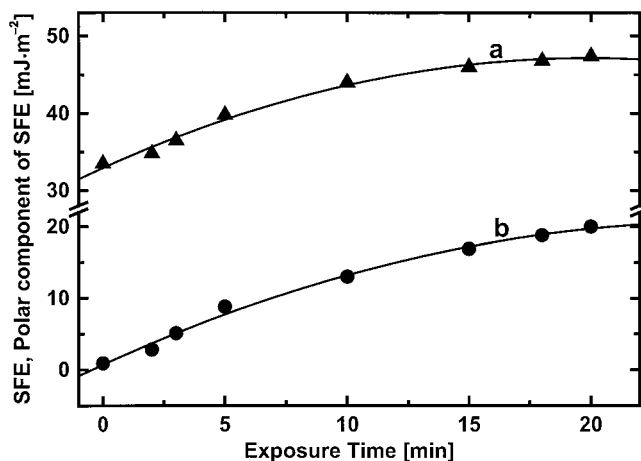


Figure 1. Variation of the SFE and its polar component for low-density PE pretreated by UV/POCl₃ with the time of UV exposure (the distance of UV source, $d = 50$ mm). a) SFE. b) Polar component of SFE.

RESULTS AND DISCUSSION

The results of adhesive properties investigation of PE pretreated by UV/POCl₃ are summarized in Figures 1–5.

Figure 1 demonstrates a nonlinear increase of the SFE (curve a) and its polar component (curve b) for low-density PE in dependence on the time of UV modification in the presence of phosphoric chloride at a distance of UV source 50 mm. The SFE of nonmodified PE reached 33.5 mJ/m². As seen in the Figure 1, the values of the SFE of PE increased nonlinearly and after 20 min of the pretreatment the value 46.8 mJ/m² was reached. This final value of the SFE of modified PE was higher compared with those obtained for isotactic polypropylene pretreated by the same procedure (12). The polar component of the SFE of modified PE increased from very low value equal to 0.9 mJ/m² for unmodified low-density PE up to 20 mJ/m² after 20 min of modification. As seen in the Figure 1, a levelling off after ~10 min of pretreatment follows the initial increase of the SFE values. This result can be explained considering the saturation of the polymeric surface by the polar functional sites during the pretreatment process.

The efficiency of UV/POCl₃ modification depends on the crystallinity degree of PE as shown in Figure 2. An UV/POCl₃ modification of high-density PE with a higher degree of crystallinity results in lower effect of the treatment compared with low-density PE. The value of the polar component of the SFE was 20 mJ/m² for low-density PE modified by UV/POCl₃ treatment for 20 min, whereas the same value for high-density PE was only 16.2 mJ/m². As expected, the modification process and, consequently, the level of hydrophilicity of PE and its adhesive properties are affected by the crystallinity of polymer. Obviously, the oxidation reaction is much more pronounced in the amorphous part of polymer as indicated by other



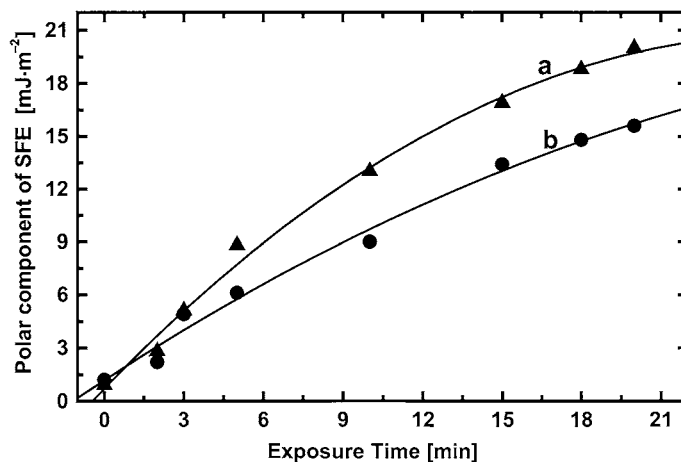


Figure 2. Variation of the polar component of the surface free energy of PE modified by UV/POCl₃ ($d = 50$ mm) with the time of UV irradiation. a) Low-density PE. b) High-density PE.

articles dealing with the PE oxidation under various conditions (14,15). The results presented in Figure 2 are in strong agreement with those measured recently for corona discharge-modified polyolefins (3).

The dependence of the polar component of the SFE of modified low-density PE on the relative intensity of UV radiation source is shown in Figure 3. The intensity of the UV radiation is inversely proportional to the square of the UV source distance from the surface of polymer. According to Figure 3, the growth of the UV radiation relative intensity leads to the increase of the polar component of the SFE. Fast growth of the polar component of the SFE with the increase of relative intensity was observed up to value $I_{rel} = 0.25$, corresponding to the distance from the UV

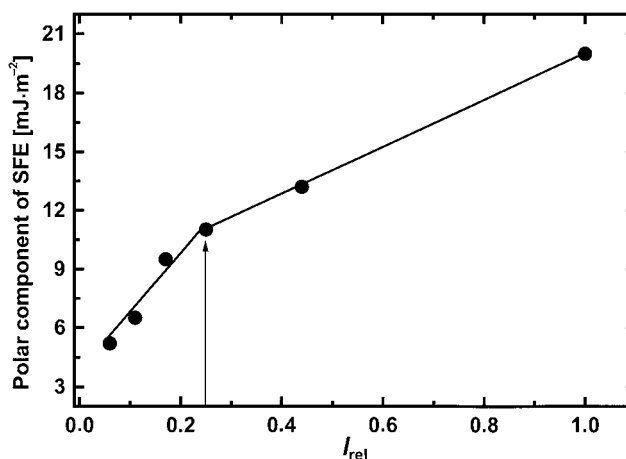


Figure 3. Variation of the polar component of the SFE of low-density PE modified by UV/POCl₃ with the relative intensity of UV radiation (the time of UV exposure, $t = 20$ min).



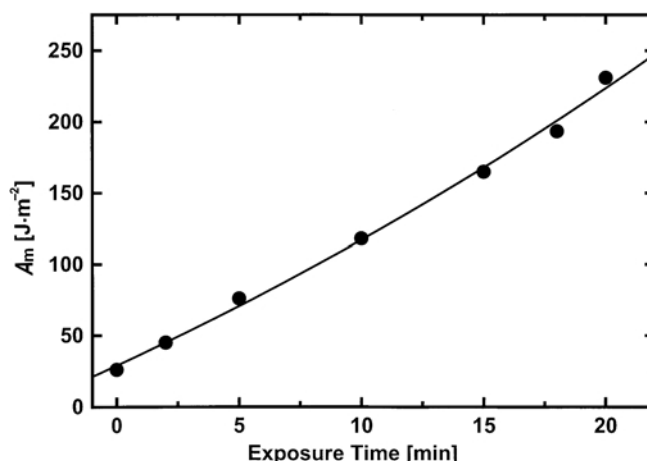


Figure 4. Mechanical work of adhesion of low-density PE pretreated by UV/ $POCl_3$ ($d = 50$ mm) to polyvinyl acetate as a function of the UV irradiation time.

radiation source $d = 100$ mm. A further increase in the relative intensity resulted in less pronounced increase of the polar component values. This phenomenon can be explained by a summation of factors such as mutual deactivation of the pairs of radicals formed by UV irradiation at higher radical concentration, saturation of the surface by polar moieties, and a decrease of the reaction rate due to diffusion effects. The increase of the relative intensity of UV radiation of UV/ $POCl_3$ modified PE from $I_{rel} = 0.06$ (the distance of UV source was 200 mm) up to $I_{re} = 1$ (the distance was 50 mm) results in a growth of the polar component of the SFE from 5 mJ/m^2 to the value near 20 mJ/m^2 .

The dependence of mechanical work of adhesion of UV/ $POCl_3$ modified low-density PE toward polyvinyl acetate on the time of UV exposure is shown in Figure 4. The mechanical work of adhesion grows almost linearly in dependence on the exposure time from 26 J/m^2 for unmodified PE up to 231 J/m^2 for the 20 min of modification. The changes in polar component of the SFE (Fig. 1) resulted in the growth of the mechanical work of adhesion to polyvinyl acetate during UV/ $POCl_3$ modification of the polymer.

The values of the mechanical work of adhesion of modified low-density PE (Fig. 4) were compared with those of the hydrophilicity measurements (Fig. 1, curve b), and the dependence is shown in Figure 5. Thus, a correlation between mechanical work of adhesion and hydrophilicity of modified PE was found. The dependence in Figure 5 was analyzed by polynomial regression. A nonlinear correlation describing the changes in the mechanical work of adhesion of UV/ $POCl_3$ modified low-density PE against polar component of the SFE is expressed according formula:

$$A_m = 30.8 + 1.4 \times \gamma \gamma_s^p + 0.4 \times (\gamma_s^p)^2, \quad r^2 = 0.99. \quad (2)$$



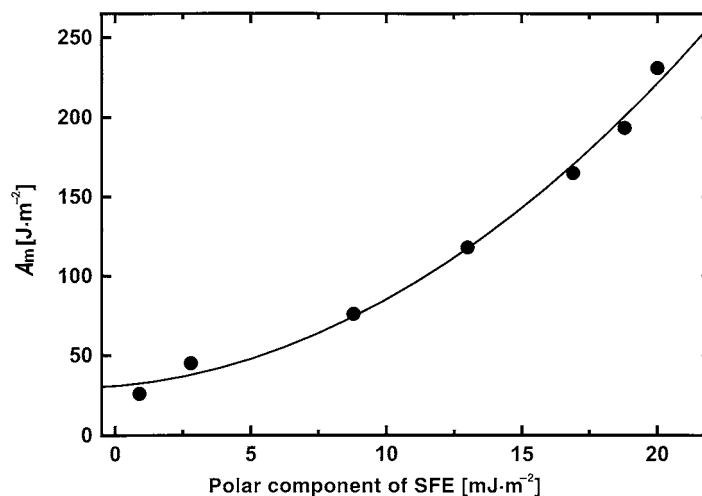


Figure 5. Mechanical work of adhesion to polyvinyl acetate of modified low-density polyethylene (UV/ POCl_3 , $d = 50$ mm) as a function of the polar component of SFE.

The value of the mechanical work of adhesion of low-density PE modified by UV/ POCl_3 can be predicted according to Equation (1), if the value of hydrophilicity is known. The growth in the polar component of the SFE by 10 mJ/m^2 leads to an increase in the mechanical work of adhesion to polyvinyl acetate by 84.8 J/m^2 . The results in Figure 5 show that hydrophilicity of modified PE is a key factor for the mechanical work of adhesion to more polar polymers.

CONCLUSION

The modification of PE by UV/ POCl_3 leads to a strong increase in the hydrophilicity and adhesive properties of the pretreated polymer compared with the unmodified polymer. A nonlinear increase of the SFE and its polar component against time of UV exposure has been observed. The efficiency of PE modification by UV/ POCl_3 depends significantly on the crystallinity of the polymer, on the intensity of the UV radiation, and also on the time of modification. The mechanical work of adhesion of modified PE to polyvinyl acetate can be calculated from the polar component of the SFE according to the empirical equation derived. The results of the adhesive properties measurements of pretreated PE are in agreement with those measured recently for isotactic polypropylene.

ACKNOWLEDGMENT

The work was supported by the Slovak grant agency VEGA (Grant 2/5032/98).



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Received February 10, 2000

Revision received July 25, 2000



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