

# Investigation of long-term hydrophobic recovery of plasma modified polypropylene

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This study concerns the surface and adhesive properties of isotactic polypropylene (iPP) modified by an electric discharge plasma and affected by long-term hydrophobic recovery of the polymer surface after modification. The investigations were focused on the change in polarity of the modified polymer expressed by the polar fraction as well as on the decrease in the surface free energy, its polar component and mechanical work of adhesion ( $A_m$ ) to polyvinyl acetate.  $A_m$  of modified iPP to polyvinyl acetate as a function of polar fraction can be described by a mathematical formula. It has been confirmed that the most intensive decrease in the surface and adhesive properties investigated is produced by the long-term hydrophobic recovery of the polymer appears in the course of the first 30 days after its modification. During subsequent aging the process of polymer hydrophobic recovery proceeds more slowly. It has been found that the value of surface and adhesive properties of iPP as well as the dynamics of the decrease in these properties during hydrophobic recovery of the surface after modification is, in the main, dependent on the iPP crystallinity. © 2004 Kluwer Academic Publishers

## 1. Introduction

Isotactic polypropylene (iPP) belongs to a group of polymers with outstanding hydrophobic properties, which are responsible for low values of surface free energy (SFE), and insufficient adhesion properties [1–3]. For practical applications (printing inks, bonding), an enhancement of the surface and adhesive properties of iPP is important. This aim can be achieved by using an appropriate modification process in the course of which some polar functional groups are introduced to the polymer macromolecules [4]. The surface modification results in increasing polarity of iPP because a thin, only a few tens of nanometers thick, layer of modified polymer is formed, while the original mechanical properties of the polymer are preserved. There are many methods of surface modification of iPP, but only some of them are suitable for the continuous processing of polymer foils [5, 6]. Some methods of surface modification are based on the action of aggressive chemical substances, e.g., chromosulfuric and nitric acid [7, 8] or chromyl chloride [9] which usually impair the final mechanical properties of the polymer. The physical methods of raising the SFE of iPP by adding low-molecular substances [10] or more polar polymers into the polymer matrix [11] also bring about a decrease in its mechanical properties. This method of modification is, to a great degree, limited by solubility of the low-molecular substances in the polymer or by compatibility of the polymer with the used polymer modifiers.

One of the most effective methods of modification of iPP foils is surface modification using an electric discharge plasma at atmospheric pressure (corona discharge) [12–16]. This method of modification allows preservation of the original mechanical properties of the iPP, provided the optimum parameters of electric discharge have been set, while the SFE and polarity increase. The insufficient stability of the polarity of such a polymer surface after modification by the electric discharge brings some difficulties, i.e., due to the fact that some instable oxygenic functional groups such as peroxidic or hydroperoxidic groups are formed and subsequently decompose to give the more stable ketonic and aldehydic groups [17, 18]. Because of thermodynamic preference, the SFE of the polymer decreases due to the transfer of polar functional groups from the surface of polymer into the bulk [19–21]. Owing to hydrophobic recovery following modification of iPP its polarity decreases and the original modification effect grows weak. The process of hydrophobic recovery takes place on the surface of the polymer after modification and is dependent on the current density used as well as on the polymer crystallinity. The decrease in polarity of the modified polymer manifests itself by a decrease in wettability of the polymer surface with polar liquids, e.g., water, glycerol, liquid polar inks etc. It is therefore important to scrutinize the process of hydrophobic recovery of iPP modified by a corona discharge plasma and to take into account this fact before further processing of the stored modified iPP films [22, 23].

This study is concerned with the kinetics of long-term hydrophobic recovery of iPP films modified by an electric discharge, based on the investigation of their surface and adhesive properties.

## 2. Experimental

In this study biaxially oriented (BO) iPP Mosten 59 492 in the form of film, thickness 0.02 mm (Chemopetrol, Czech Republic):  $\rho_{25^\circ\text{C}} = 0.916 \text{ g} \cdot \text{cm}^{-3}$ ,  $T_m = 171^\circ\text{C}$ ,  $\Delta H_{\text{melt}} = 94.4 \text{ J} \cdot \text{g}^{-1}$  and extruded iPP Mosten 52 516 in the form of film, thickness 0.02 mm,  $\rho_{25^\circ\text{C}} = 0.905 \text{ g} \cdot \text{cm}^{-3}$ ,  $T_m = 165^\circ\text{C}$ ,  $\Delta H_{\text{melt}} = 43.4 \text{ J} \cdot \text{g}^{-1}$  were used.

The adhesive joints of modified iPP were prepared by using a solution of polyvinyl acetate (Polysciences, USA) in ethyl acetate (Fluka, Germany). The modification of iPP films by the electric discharge was performed in a pilot plant Softal 2005 (Softal, Germany) in air at atmospheric pressure at a temperature of 295 K. The mechanical work of adhesion was found by peeling the adhesive joints at an angle of  $90^\circ$  using a universal testing machine (Instron 4301, England). The measurements were carried out on a peeling wheel in which the adhesive joints (20-mm wide and 140-mm long) were fixed. The SFE was measured with a microscopic goniometer (Zeiss, Germany) by determining the contact angles  $\Theta$  of testing liquids of different polarity on the polymer surface as a function of time 't' and extrapolating to  $t = 0$ . The mathematical relationships used for calculating the mechanical work of adhesion and free surface energy or its polar and dispersive components have been presented in previous publications [9, 10].

## 3. Results and discussion

Variation of SFE and its polar component with time after modification is represented in Fig. 1 for BO iPP modified by the electric discharge. During aging the hydrophilicity of the modified BO iPP films initially dropped. The decrease in hydrophilicity (Fig. 1) manifested itself by a non-linear fall in the total SFE (plot a) as well as the polar component of SFE (plot b). 30 days

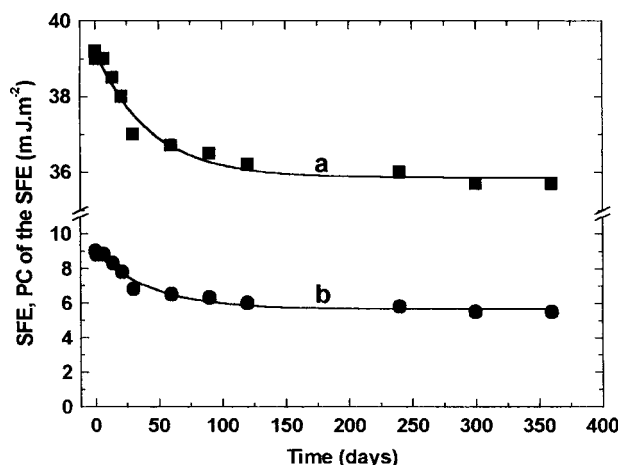


Figure 1 SFE and its polar component for BO iPP modified by the discharge plasma during long-term hydrophobic recovery: (a) SFE and (b) polar component of SFE.

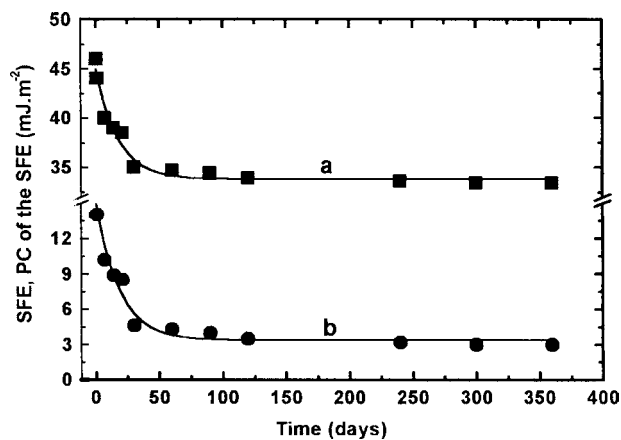


Figure 2 SFE and its polar component for extruded iPP modified by the discharge plasma during long-term hydrophobic recovery: (a) SFE and (b) polar component of SFE.

after modification the value of total SFE had fallen from 39.2 to 37.0  $\text{mJm}^{-2}$ . A greater relative decrease was observed for the polar component of SFE, which fell from 9.2 to 6.8  $\text{mJ} \cdot \text{m}^{-2}$  in the course of 30 days after modification. In the course of further aging the process of iPP hydrophobization proceeded rather move slowly and after 360 days SFE and its polar component reached 35.7 and 5.5  $\text{mJ} \cdot \text{m}^{-2}$ , respectively. From these values, one year after modification of the BO iPP by the electric discharge, the total SFE decreased only a little (9%), while the polar component of the SFE fell up to 40% when compared with that of a freshly modified sample. The measurements of the SFE and its polar component of SFE for the BO iPP modified by the corona discharge show that the total SFE and its polar component decreased while the dispersive component of SFE of the modified polymer remained practically unchanged.

Dependence of the SFE and the polar component of SFE on long-term aging are represented in Fig. 2 for extruded iPP modified by the electric discharge. In comparison with BO iPP the hydrophobic recovery of extruded iPP films subjected to modification by the electric discharge was much more obvious and the total SFE (plot a) and its polar component (plot b) fell particularly in the course of the first 30 days after modification, in the same manner as observed for BO iPP. According to Fig. 2 the decrease in the hydrophilicity of extruded iPP manifested itself by a non-linear decrease in the SFE and the polar component of SFE. While the value of the total SFE dropped significantly from 46 to 35  $\text{mJ} \cdot \text{m}^{-2}$ , the polar component of the SFE declined still more in this interval, i.e., from 15.8 to 4.6  $\text{mJ} \cdot \text{m}^{-2}$ . In the course of further aging of the extruded iPP the process of hydrophobic recovery of modified surface became slower and after 360 days the values of the SFE and its polar component attained 33.4 and 3  $\text{mJ} \cdot \text{m}^{-2}$ , respectively. On this basis, the total SFE of the modified extruded iPP decreased by 24% after 30 days and 27% after 360 days following modification. On the other hand, the polar component of the SFE decreased by 71% after 30 days, and by 81% after 360 days when compared with original modified sample. If we compare the values of the SFE and its polar component obtained for the BO iPP and the extruded iPP modified

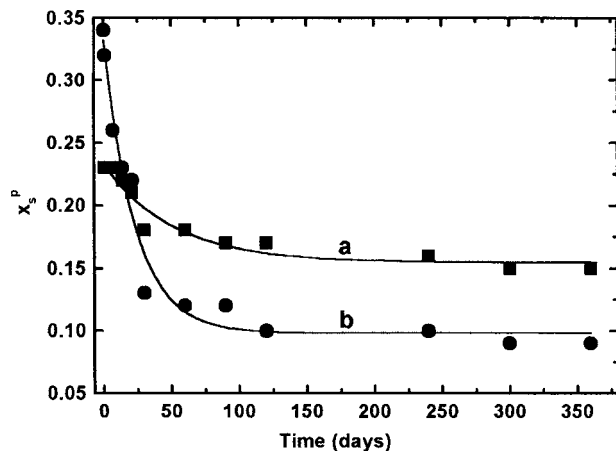


Figure 3 Polar fraction of the iPP surface modified by the electric discharge during long-term hydrophobic recovery: (a) BO iPP and (b) extruded iPP.

by the corona discharge, we can conclude that the extruded iPP exhibits essentially higher dynamics for the hydrophobic recovery process than BO iPP. This difference is attributed to the difference in the crystallinity of extruded and BO iPP. The functionalization of iPP due to linking polar functional groups to the polymer chain during modification takes place in the amorphous phase of the polymer. This is more significant in the case of extruded iPP, which has lower crystallinity compared with BO iPP. Owing to this lower crystallinity of modified extruded iPP a higher polymer polarity and thus a higher value of SFE results. Fig. 3 depicts the polar fraction for BO iPP (plot a) and for extruded iPP (plot b) after modification by the electric discharge in the process of long-term hydrophobic recovery.

According to Fig. 3 both relationships exhibit non-linear character and the marked decrease in the case of extruded iPP amounted to 62% after 30 days and after 360 days following modification it was 74%. A slight decrease in hydrophilicity was observed after modification of BO iPP, i.e., the polar fraction was reduced by 22% after 30 days and 35% after 360 days following treatment. The greatest decrease in the polar fraction of iPP modified by the electric discharge was observed over 30 days after modification and during further aging the decrease was rather less for both extruded and BO iPP. If we compare plot a with plot b in Fig. 3, we can state that the decrease in the polar fraction for extruded iPP modified by the electric discharge and exposed to long-term aging was twice that of BO iPP.

Fig. 4 presents the dependence of the mechanical work of adhesion,  $A_m$ , for an adhesive joint with polyvinyl acetate on aging the modified BO iPP (plot a) and extruded iPP (plot b). In the course of aging of the iPP films,  $A_m$  fell in a non-linear manner. After 360 days of aging  $A_m$  fell 26% for modified BO iPP when compared with original value of  $A_m$  and by 52% for modified extruded iPP. As for the polar fraction the greatest decrease in  $A_m$  produced by hydrophobic recovery of the surface of modified iPP was observed after 30 days following modification. During further aging a significant decrease in  $A_m$  was also observed.

As there is an apparent correlation between  $A_m$  and the polar fraction found for iPP modified by the electric

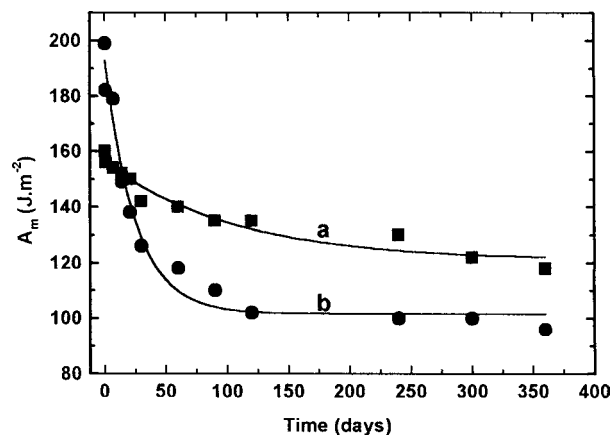


Figure 4 Mechanical work of adhesion to polyvinyl acetate for iPP modified by the electric discharge during long-term aging: (a) BO iPP and (b) extruded iPP.

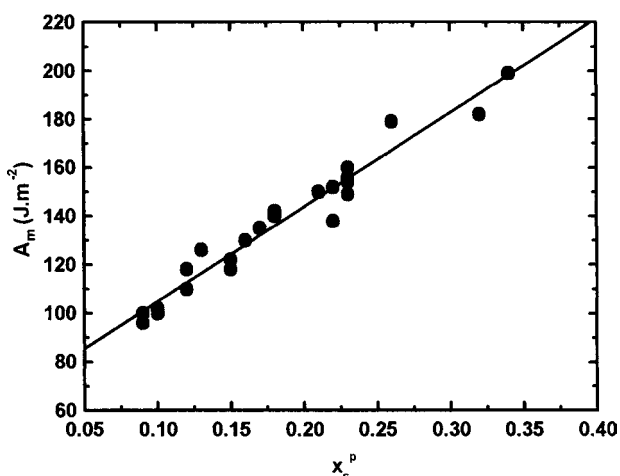


Figure 5 Dependence of the mechanical work of adhesion to polyvinyl acetate for iPP modified by discharge plasma on polar fraction.

discharge  $A_m$  has been plotted as a function of polar fraction (Fig. 5). The relationship is linear and can be described by the equation:

$$A_m = 65.9 + 3.9 \times 10^2 \cdot x_p^s, \quad r = 0.99$$

The relative decrease in the strength of adhesive joints of the modified iPP to polyvinyl acetate arising during the process of hydrophobic recovery is represented in Fig. 6 for BO iPP (plot a) and extruded iPP (plot b) modified by the electric discharge. According to Fig. 6 the decrease in adhesive properties is significantly smaller for BO iPP when compared with that of the extruded iPP in contradiction with assumptions based on the values found of the polar component of the SFE. The decrease in values of the polar component of SFE, the polar fraction and the mechanical work of adhesion for iPP modified by the electric discharge may be attributed to the successive destruction of unstable oxygenic functional groups (peroxides and hydroperoxides) arising in the initial stage of modification which give rise to the formation of more stable products. The process of hydrophobic recovery after iPP modification results from the tendency of the polymer to reduce the SFE because of the thermodynamic preferences present and thus to

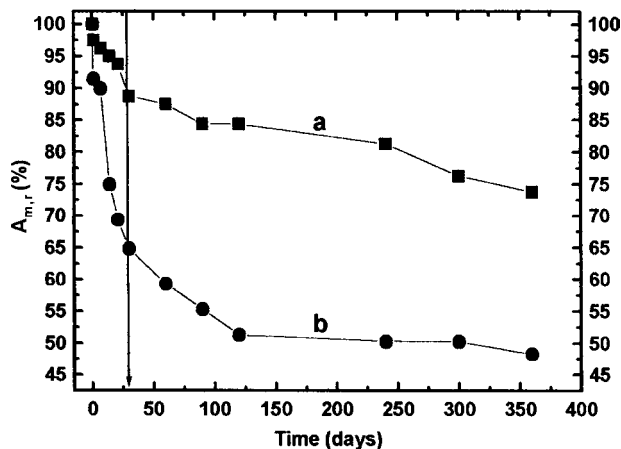


Figure 6 Variation of the relative change in the strength of the adhesive joint in the system modified iPP—polyvinyl acetate during long-term hydrophobic recovery: (a) BO iPP and (b) extruded iPP.

rearrange the polar functional groups in the direction of polymer bulk. Because of this, the degree of surface modification of iPP by the electric discharge is, to certain extent, dependent on the crystallinity of the polymer and on time elapsed after polymer modification.

#### 4. Conclusions

The investigation of the influence of long-term aging of iPP exposed to modification by an electric discharge plasma on the surface and adhesive properties has shown that the dynamics of the hydrophobic recovery process is to a high degree dependent on polymer crystallinity. Thus BO iPP, showing higher crystallinity, acquires a considerably higher stability of the surface after modification by the electric discharge in contrast to extruded iPP, which shows lower crystallinity. The initial values of the polarity and the mechanical work of adhesion were significantly higher for the extruded iPP modified by the electric discharge when compared with BO iPP. It appears that the final values of the polarity and the mechanical work of adhesion are higher for the modified BO iPP exposed to long-term aging than those observed for extruded iPP, which can be attributed to the higher crystallinity of BO iPP in comparison with that of extruded iPP.

#### Acknowledgements

This study was accomplished with financial support of Slovak Grant Agency VEGA, grants No 2/1060/21 and 2/1029/21.

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Received 23 April  
and accepted 3 December 2003