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# Study of Adhesion and Surface Properties of Modified Polypropylene

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## 1. Introduction

Isotactic polypropylene (iPP) is one of the most frequently applied polymers. Unfortunately, it has a disadvantage of being non-polar which makes the adhesive joints formed with other, more polar polymers, rather weak (Brewis & Mathieson, 2002; Chodák & Novák, 1999; Pocius, 1997; Kinloch, 1987; Schultz & Nardin, 1994; Kolluri, 1994; Denes & Manolache, 2004). From the point of view of application of iPP it is desirable that their adhesive properties are improved (Yalozis et al., 2000; Ohare et al., 2002; Shenton et al., 2001; Kim et al., 2002; Moosheimer & Bichler, 1999). This demand can be met by a modification of iPP, while polymer can be modified either at the surface directly, e.g. by plasma or electric discharge (Denes & Manolache, 2004), or in bulk, by addition of a suitable polar low- or high-molecular compound to the polymeric matrix (Novák & Florián, 1994; Novák et al., 2004; Novák & Florián, 2001; Novák, 1996). The presented contribution aims at offering the efficient methods of surface modification of iPP, from the point of view of improving its adhesion properties. Recent achievements will be discussed to evaluate physical and chemical changes taking place as a result of modification.

The analysis of the low adhesive properties of iPP leads to the two different approaches of explanation (Brewis & Mathieson, 2002; Chodák & Novák, 1999; Kinloch, 1987). By the first explanation the low adhesion of iPP consists in a formation of thin layer of low-molecular substances on the interfacial boundary. The primary function of modification is then a removal of the thin low-molecular substance layer from the polymer surface, while the chemical modification itself is of a secondary importance. The second explanation attributes the low adhesive properties of iPP to its non-polar character and low surface energy, stressing the dependence of the adhesive properties of iPP on their super molecular structure. The chemical changes resulted in the increase of the polarity and surface energy are considered for the most important in the modification of iPP.

Low-molecular substances present in iPP (Brewis & Mathieson, 2002; Kinloch, 1987) such as antioxidants, lubricants, impurities introduced into polymer during polymerization process, the ends of polymer chains originating from the initiator, as well as impurities introduced into polymer during granulation and foil processing reduce the strength of adhesive joints due to their low cohesion. After removing the low-molecular substances by precipitation, the resulting polymer dispatched the higher adhesive properties. For iPP with

wide distribution of molecular masses polymer-homologues with lower molar mass and higher mobility penetrate to the region of interfacial boundary by diffusion, reducing thus the interfacial tension. As a result of the thermal and Brown's motions, the interfacial boundary is enriched by oligomers and the value of the surface energy is reduced. In the region of iPP surface after cross linking in inert atmosphere by UV irradiation short polymer chains became cross linked removing thus the thin adhesion reducing layer of low-molecular substances on the interfacial boundary and as a result of this modification an increase of adhesive properties was observed.

iPP as a non-polar polymer has a very low (near zero) value of the polar component (PC) of the surface energy (Brewis & Mathieson, 2002; Chodák & Novák, 1999). When the polarity of iPP is increased also the value of the surface energy and its PC are increased as well. The growth of iPP polarity can be reached by utilization of some of existing methods of modification (Kinloch 1987), e.g. by flame modification. In the course of modification of iPP suitable polar functional groups are introduced. This process results into an increase of the compatibility of iPP with the polar polymers and the growth of its adhesion. Increasing the polarity of iPP can also be obtained by the addition of polar low-molecular substances or polymer to the matrix of iPP. In the case of this modification the increase of adhesion is to a large extent caused by an increasing mobility of polymer chains, e.g. by addition of fatty acids and their salts or oxidized and/or maleic anhydride grafted paraffin wax to iPP. From the point of view of the diffusion theory of adhesion (Schultz & Nardin, 1994) it is the kinetic effect taking part in this increase.

The iPP has in comparison with low-density polyethylene a higher degree of crystallinity (Brewis & Mathieson, 2002; Kinloch, 1987). During crystallization of iPP a smectic or a crystalline monoclinic form is formed depending on the thermal history of the sample. The smectic form is relatively stable up to temperature 50 °C; at higher temperature it is transformed into the monoclinic crystalline form. It was experimentally proved that the adhesive properties of monoclinic crystalline form are higher than those of smectic form, while the value of the surface energy of iPP grows with the degree of changes from smectic form to monoclinic crystalline form.

The presence of low-molecular substances in iPP results in a formation of thin layer on the interfacial boundary decreasing the value of the surface energy. This effect prevails over the effect of increasing surface energy during the change of smectic form to crystalline monoclinic form and thus the adhesion of iPP is decreased after conditioning of adhesive joints at the temperature of 50 - 90 °C. The increased adhesion of iPP can be reached by heating the polymer above the temperature of 170 °C (or above the melting point of iPP) and subsequent fast cooling. Utilization of this procedure inhibits formation of the thin interfacial layer of low-molecular substances and iPP crystallized in the smectic form.

During the surface modification of iPP the structure of its surface changes and becomes rough. The changes of the surface structure during the modification of iPP depend on the applied modification method and on the thermal history of the polymer sample. It was found that there is a linear relationship between the roughness of the polymeric surface and the value of the mechanical work of adhesion. An increase of the mechanical properties of iPP is in this case related to mechanical fixation of adhesive in pores, or to micro defects of the polymeric surface. The change of the physical character of the surface takes place also in modification of iPP in mass by addition of suitable additives increasing iPP adhesion accompanied by simultaneous changes of super molecular structure of polymer.

IPP relatively easily undergoes the oxidation (Chodák & Novák, 1999). This is observed under the effect of light, heat, UV irradiation, plasma or electric discharge and oxidation agents while functional groups are formed which are capable of participating in the further chemical reactions (Brewis & Mathieson, 2002; Kinloch, 1987; Kolluri, 1994). In the course of oxidation of iPP hydroperoxide, carbonyl, carboxyl and hydroxyl groups are formed. In previous studies a formation of ozonides and peroxides during oxidation has been observed. In the case of halogenization methods of iPP modification halogens are attached to the polymer chain, and are often combined with the oxygen.

## 2. Experimental

### 2.1 Used polymers

For corona discharge modification experiments these sorts of iPP have been used:

- biaxially oriented foils of iPP Mosten 59 4928 (Chemopetrol, Czech Republic): thickness = 0.02 mm, density (23 °C) = 0.956 g.cm<sup>-3</sup>,  $T_{\text{melt}} = 170\text{ °C}$ ,  $\Delta H_{\text{melt}} = 94.4\text{ J.g}^{-1}$ . Extruded iPP of 0.02 mm thickness (Chemopetrol, Czech Republic): density (23 °C) = 0.905 g.cm<sup>-3</sup>,  $T_{\text{melt}} = 165\text{ °C}$ ,  $\Delta H_{\text{melt}} = 49.4\text{ J.g}^{-1}$ . iPP backing fabric produced from Mosten 58 512 (Chemopetrol, Czech Republic) containing 0.2 wt.% of 2,6-di(tertbutyl)-1,4-dimethylphenol: density (23 °C) = 0.920 g.cm<sup>-3</sup>,  $T_{\text{melt}} = 162\text{ °C}$ ,  $\Delta H_{\text{melt}} = 89.7\text{ J.g}^{-1}$ . Aqueous dispersion of butyl acrylate-vinyl acetate copolymer Duvilax KA-31 (Duslo, Slovakia) containing 53.1 wt.% of dry content, pH = 4 - 6, content of free monomer 0.9 wt.%, viscosity 10 - 70 mPa.s<sup>-1</sup>, was used as a polymer deposit on iPP backing fabric.

For grafting experiments were used these polymers as following:

- stabilised iPP Mosten 58 512 (Chemopetrol, Czech Republic) containing 0.2 wt.% of 2,6-ditertbutyl-1,4-dimethylphenol: density (23 °C) = 0.920 g.cm<sup>-3</sup>,  $T_{\text{melt}} = 162\text{ °C}$ ,  $\Delta H_{\text{melt}} = 89.7\text{ J.g}^{-1}$ , polyamide Silamid 30 SW13 (PCHZ, Slovakia), polyvinyl acetate (Polysciences, USA) and cellulose acetate (Czech Republic), aluminum (Slovakia).

For modification by chromyl chloride and chromo sulfuric acid a stabilized polymer iPP Tatren TF- 411,  $M_v = 2.16 \cdot 10^5$  (Slovnaft-Mol, Slovakia) was used.

The halogenization experiments were performed using a commercial iPP:

- iPP Tatren FD 420 containing 0.2 wt.% of UV stabilizer (Slovnaft-Mol, Slovak Republic), MFI = 3.2 g/10min, density (23 °C) = 0.905 g.cm<sup>-3</sup>, polyvinyl acetate,  $M_w = 1.6 \times 10^5\text{ g.mol}^{-1}$  (Polysciences, USA).

### 2.2 Measurements methods

#### 2.2.1 Contact angles and surface energy

The values of contact angles were determined by direct goniometric measurement using a Contact Angle Meter Amplival Pol (Zeiss, Germany). The drops of testing liquid ( $V = 3\text{ }\mu\text{l}$ ) were introduced onto the polymeric surface. Each measurement was carried out with a set of the testing liquids: glycerol, formamide (Serva, Germany), thio diglycol, ethylene glycol,  $\alpha$ -bromo naphthalene (Aldrich, USA), methylene iodide (Fluka, Switzerland), benzyl alcohol, diethylester of anthranil acid (Merck, Germany), twice distilled water. Each

measurement was repeated 5 times at 25 °C and the dependencies  $\theta = f(t)$  were extrapolated to  $t = 0$ . The dispersive and PC of the surface energy of polymer were calculated according to the relation (47-50):

$$\frac{(1 + \cos \theta) \cdot (\gamma_{LV}^d + \gamma_{LV}^p)}{2} = (\gamma_{LV}^d \cdot \gamma_s^d)^{1/2} + (\gamma_{LV}^p \cdot \gamma_s^p)^{1/2} \quad (1)$$

where  $\theta$  is the contact angle (deg),  $\gamma_{LV}^d$ ,  $\gamma_{LV}^p$  is the polar and dispersive component of the surface energy of testing liquid (mJ.m<sup>-2</sup>), while

$$\gamma_s^{\text{total}} = \gamma_s^p + \gamma_s^d \quad (2)$$

where  $\gamma_s^{\text{total}}$  is the total surface energy and  $\gamma_s^p$ ,  $\gamma_s^d$  is the polar and dispersive component of the surface energy of polymer (mJ.m<sup>-2</sup>).

### 2.2.2 Interfacial equilibrium work of adhesion and interfacial tension

Interfacial equilibrium work of adhesion was calculated using the values of polar and dispersive components of the surface energy according to the relation:

$$W_{a1,2} = \frac{4 \cdot (\gamma_1^d + \gamma_2^d)}{\gamma_1^d + \gamma_2^d} + \frac{4 \cdot (\gamma_1^p + \gamma_2^p)}{\gamma_1^p + \gamma_2^p} = W_{a1,2}^d + W_{a1,2}^p \quad (3)$$

$$\gamma_{1,2} = \gamma_1 + \gamma_2 - W_{a1,2} \quad (4)$$

where  $W_{a1,2}^d$  and  $W_{a1,2}^p$  are the dispersive and polar component (PC) of interfacial equilibrium work of adhesion, (mJ.m<sup>-2</sup>),  $\gamma_1^d$ ,  $\gamma_2^d$  are the dispersive components of the surface energy of the polymer 1 and 2 respectively (mJ.m<sup>-2</sup>),  $\gamma_1^p$ ,  $\gamma_2^p$  are the PC of the surface energy of the polymer 1 and 2 respectively (mJ.m<sup>-2</sup>),  $\gamma_{1,2}$  is the interfacial tension between polymer 1 and polymer 2 (mJ.m<sup>-2</sup>).

### 2.2.3 Mechanical work of adhesion by peeling

The mechanical work of adhesion was measured by peeling of adhesive joints using an 5 kN universal testing machine Instron 4301 with a peeling wheel with adjustable angle of peeling 90° at speed 10 mm.min<sup>-1</sup>. The adhesive joints have been prepared by the application of polyvinyl acetate from ethyl acetate solution onto the technical cotton fabric "Molino" using a coating pad Dioptra (Czech Republic). The iPP foil and impregnated cotton fabric have been fixed together and the adhesive joints have been dried at 60 °C to a constant weight, then they were cut to strips with dimensions 25 x 200 mm. The peeling length of an adhesive joint was 100 mm. The values of mechanical work of adhesion  $A_m$  (J.m<sup>-2</sup>) were calculated by equation:

$$A_m = F_s / b \quad (5)$$

where  $F_s$  is the medium peeling force (N) and  $b$  is the width of the adhesive joint (m).

Measurements were carried out using a software developed for universal testing device Instron, Series IX.

### 2.2.4 Strength of adhesive joint by shear

The strength of adhesive joint was determined by testing of single overlapped adhesive joints in shear using a dynamometer Instron 4301 with aluminum slabs having dimensions 10 x 60 mm, the thickness was 2 mm, the length of overlapping area was 15 mm and the thickness of deposited adhesive was 0.1 mm.

### 2.2.5 Molecular weight

The molecular weight of iPP was determined on a high-temperature viscometer heated with silicone oil. The viscosity of iPP was measured in  $\alpha$ -chloro naphthalene at 145 °C. The molecular weight was calculated from the following equation:

$$[\eta] = 4.9 \cdot 10^{-3} \cdot M_v^{0.80} \quad (6)$$

where  $[\eta]$  is limiting viscosity number (dl.g<sup>-1</sup>) and  $M_v$  is molecular weight of polymer obtained viscometrically.

### 2.2.6 ESR analysis

iPP modified by chromyl chloride was subjected to electromagnetic spin resonance measurements using a spectrophotometer E4. The following parameters were applied: frequency 100 kHz, microwave power 200 mW, resolution 100 mG, sensitivity  $5 \times 10^{10}$  spin.G<sup>-1</sup>. The relative concentration of Cr<sup>IV</sup> was calculated according to the equation:

$$C_{\text{rel}} = \frac{I \cdot \Delta H^2}{m \cdot s} \quad (7)$$

where I, H, m and s are intensity of spectrum, width of band, amount of weighed sample and sensitivity of device respectively.

### 2.2.7 Hydroperoxides determination

Hydroperoxides content was determined spectrophotometrically. A sample of modified iPP was kept for 12 hours in vacuum for removing the physically adsorbed oxygen. Acetic acid and n-heptane were distilled and nitrogen was allowed to bubble through solutions. Then 3 ml of saturated solution of potassium iodide in isopropyl alcohol, 1 ml of glacial acetic acid and 1 ml of n-heptane were placed into a 10 ml Erlenmeyer flask.

The samples of foils of the modified iPP (2 x 2 cm) were put into the solution and left for 24 hours in inert atmosphere of carbon dioxide (dry ice). The absorbance at  $\lambda = 365$  nm was measured with respect to blank experiment by using a UV spectrometer. The concentration of hydroperoxides was calculated from the expression:

$$A = \varepsilon \cdot c \cdot d \quad (8)$$

where A,  $\varepsilon$ , c and d are the absorbance, molar extinction coefficient ( $\varepsilon = 25 \times 10^3$  kg.mol<sup>-1</sup>.cm<sup>-1</sup>), concentration of hydroperoxides (mol O<sub>2</sub>.kg<sup>-1</sup> polymer) and thickness of absorption cell (cm) respectively.



### 2.2.8 Carbonyl groups determination

The method of determination of carbonyl groups in oxidized iPP was based on UV spectrophotometric determination of 2,4-dinitrophenylhydrazones by means of the absorption band at  $\lambda = 365$  nm. Hydrazones originated in the reaction of oxidized iPP with 2,4-dinitrophenylhydrazine.

The reagent solution included 1 g of 2,4-dinitrophenylhydrazine, 100 ml of ethanol, 5 ml of hydrochloric acid and 5 ml of distilled water. Before each measurement a fresh solution of 2,4-dinitrophenylhydrazine was prepared. The formation of hydrazones proceeded at 70 °C in the course of 20 minutes. Then iPP was repeatedly washed with hot ethanol and perfectly dried. The disappearance of the infrared absorption bands corresponding to carbonyl groups supports the assumption that these groups were quantitatively consumed in the reaction with 2,4-dinitrophenylhydrazine.

The reaction with 2,4-dinitrophenylhydrazine finished the modified iPP was used for molding the foils that were liable to UV spectrophotometric measurements. Di (heptadecyl) ketone was used as model substance. It was added in the amount of 1wt.% to iPP, exposed to the reaction with 2,4-dinitrophenylhydrazine and thus a sample of standard was formed. According to the Beer's law it is valid:

$$\varepsilon = \frac{A_1}{c_1 \cdot d} \quad (9)$$

where  $\varepsilon$ ,  $A_1$ ,  $c_1$  are stand for extinction coefficient, absorbance, the known concentration of carbonyl groups in sample of standard and width of foil, respectively.

The value of extinction coefficient calculated from equation (9) was used for calculation of the concentrations of carbonyl groups:

$$c_x = \frac{A_x}{\varepsilon \cdot d} \quad (10)$$

where  $A_x$ ,  $c_x$  and  $d$  are absorbance of the investigated sample, the determined concentration of carbonyl groups and the width of the foil, respectively.

## 2.3 Modification methods

### 2.3.1 Modification by corona discharge

The modification of polypropylene foils by corona discharge was performed in a pilot plant (Softal 2005, Germany) in the medium of air oxygen at atmospheric pressure and temperature of 295 K. The used cylindrical electrodes were of 98 mm. The electrode voltage was equal to 9000 V and current density varied in the range among 0.3 and 0.8 mA.

### 2.3.2 Grafting by itaconic acid (IA)

Grafting of onto iPP was performed in an extruder in the polymeric melt at 220 °C during 180 sec. Itaconic acid (IA) concentration was up to 5 wt.%. Benzoyl peroxide (Aldrich, England) was added as an initiator and its concentration varied between 0.1 and 1 wt.%. Unreacted IA was then removed by Soxhlet extraction in boiling n-heptane. Pellets of IA

modified iPP have been obtained. The pellets were compression molded at 210 °C to films 0.05 mm thick suitable for goniometric measurements of contact angles.

### 2.3.3 Oxidation by chromyl chloride and chromo sulfuric acid

The modifications of iPP by chromyl chloride was accomplished in chromyl chloride vapor. The samples of iPP were individually prepared in Petri dishes and processed at individual temperatures by using particular reaction times. The reactions of oxidized iPP with 2,4-dinitrophenylhydrazine took place in a solution containing 1 gram of 2,4-dinitrophenylhydrazine as well as hydrochloric acid, ethanol and water in volume ratio 5 : 100 : 5.

Powdered iPP was modified by chromo sulfuric acid comprising sulfuric acid 96 %, potassium dichromate and water in weight ratio 100 : 5 : 8. Different reaction times and different temperatures were used for this method of modification.

### 2.3.4 Halogenization by UV/ phosphoryl chloride

The LDPE 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 PO 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  $\lambda = 366$  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:

$$I_r = \frac{I}{I_0} = (d_0/d)^2 \quad (11)$$

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

## 3. Results and discussion

### 3.1 Modification by corona discharge

During the modification of iPP by electric discharge plasma the surface of polymer interacts with the particles of plasma (Yalizi et al., 2000; OHare et al., 2002; Shenton et al., 2001; Kim et al., 2002; Novák et al., 2004; Noeske et al., 2004; Guimond et al., 2002; Mikula et al., 2003; Strobel et al., 2003; Poncin-Epaillard, 2002; Štefečka et al., 2003; Ráhel et al., 2003; Lehocký et al., 2003; Drnovská et al., 2003; Kuzuya et al., 2003). The active particles of plasma can originate either from the electric discharge at the atmospheric pressure (corona discharge) in air or from high (radio) frequency (RF) discharge at lower pressure in an inert atmosphere, or other atmosphere. The active particles of discharge plasma transferring the energy during the modification are ionic and neutral particles, electrons and UV radiation. Energy captured from the particles by the surface initiates chemical reactions leading to changed polarity and adhesion properties of iPP. The effect of plasma on the polymer surface includes the act of photons of UV irradiation having important role during the formation of



radicals. Electrons and ions do not participate in the surface modification directly but are crucial for the formation of excited atoms and molecules in the volume of the discharge and these particles in contacts with the surface induce a formation of free radicals and chemical reactions. In the interaction of polymer surface with discharge plasma of inert gas, O, N, or the air the following reactions are effective (Kinloch, 1987; Kolluri, 1994):

a) direct reactions of active particles of plasma (surface oxidation by oxygen atoms in oxygen plasma or in the air), b) creating of free radicals and their consequent reactions (polymer degradation, grafting copolymerisation, incorporation of oxygen). The oxidation effect of corona discharge on the surface of the polymer can be schematically represented by following equations:

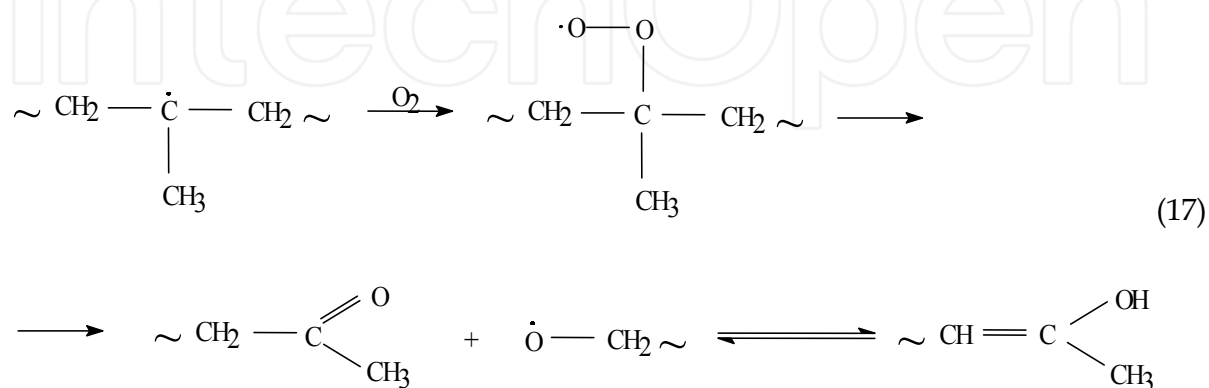


Equation (12) represents a dissociation enabled by the absorption of dissociation energy of oxygen and equation (13) of dissociation by absorption of UV energy.

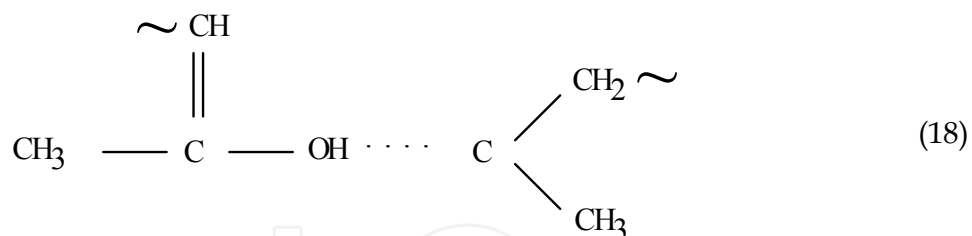
During the modification of iPP by the discharge plasma following reactions take place:



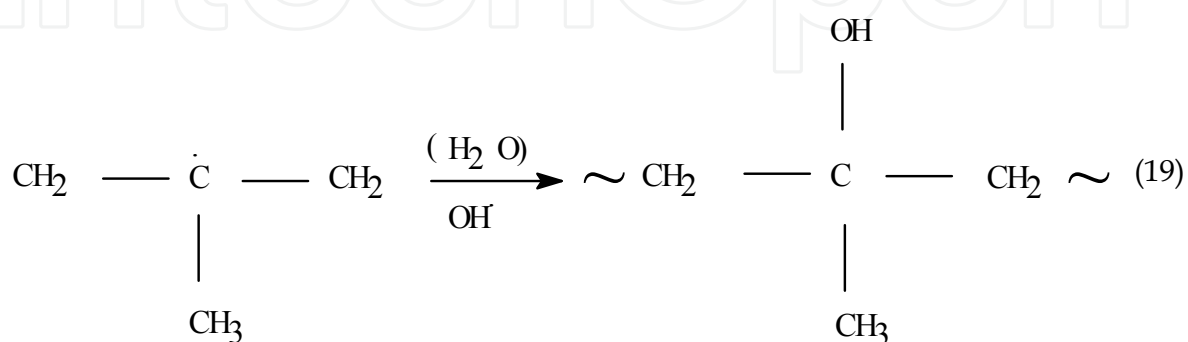
Equations (14) and (15) represent the formation of hydroperoxides during the modification, equation (16) on the other hand represents the decomposition of hydroperoxides and the formation of carbonyl groups. For the modification of iPP the modification by corona discharge at atmospheric pressure as well as a high-frequency discharge with frequency 13.56 MHz at low pressures (RF discharge) is used most often. The following scheme to represent the effect of corona discharge on iPP has been proposed:



whereupon between enolic hydrogen of enolyzed ketogroup and other ketogroup in the macromolecule hydrogen bonds are formed.



In the case of humid environment during the corona treatment of iPP the reaction of radical with oxygen is competing with a reaction of radical with water according to the scheme:



at which compounds are formed which do not contribute to the adhesive joint. A stronger decay was observed for the iPP polymerized in the discharge plasma than for that prepared by a conventional method.

The adhesion properties of iPP modified by high-frequency electric discharge in the air, oxygen and in nitrogen have been studied (Strobel et al., 2003). It was observed that after 30 seconds of exposure of the polymer in oxygen plasma the concentration of hydroperoxides reached  $1.6 \times 10^{-5} \text{ mol O}_2/\text{kg}^{-1}$  iPP and the contact angle of redistilled water decreased from  $94^\circ$  to  $40^\circ$ . By further treatment by plasma the changes in contact angles periodically oscillated around the value  $52^\circ$ , while by the aging of treated samples the contact angle was increasing.

An important group of electric discharge methods is the modification by corona discharge (Yalızis et al., 2000). The treatment of iPP by corona discharge is strongly affected by humidity. By identification of chemical changes in iPP modified in dry air via ATR spectroscopy the presence of following functional groups was shown: C=O, OH, C=C, and COOH, and observed  $>\text{C}=\text{O}$  group to reach the highest concentration. The PC of the surface energy of iPP modified by corona discharge increased non-linearly with the degree of modification while the dispersion component is practically not changed. A decrease of temperature during the modification leads to a decrease of PC of the surface energy.

The adhesive properties of iPP modified by corona discharge are decreasing if a polymer surface makes contact with a compound forming the hydrogen bonds (most often a liquid). The formation of adhesive forces on the modified surface of iPP is related to the hydrogen bond of enolic group on one polymer surface and a similar polar group (e.g. carbonyl) on the other polymer surface and by heating up the surface or by the effect of heat formed by friction one can cancel the effect of modification and original good adhesive properties decrease.

The correlation between the adhesion of corona discharge modified iPP and the formation of hydroperoxides has also been studied (Novák & Florián, 2001; Novák & Florián, 2004). A linear increase of concentration of hydroperoxides and the PC of the surface energy with the current density of corona discharge has been found. At the same time it was shown that the efficiency of the surface treatment was strongly influenced by the super molecular structure of iPP: for extruded iPP foil a higher adhesion was found than for a biaxially oriented one. Furthermore by the study of a time elapsed from the modification they found that the adhesion of extruded polymer decreases with the time while the adhesion of biaxially oriented iPP does not vary with the time. The detail analysis of chemical changes of iPP modified by corona discharge is given also by other authors whose point to the fact that the reactive groups formed at the surface modification can participate in the further reactions.

A significant increase of adhesion of iPP was obtained by grafting a suitable monomer such as acryl amide (Novák & Florián, 1995) on the surface of iPP modified by discharge plasma. A very effective is the grafting mechanism with free radicals of the polymer in the case when the free radicals are formed relatively slowly. For the surface energy of biaxially oriented iPP modified by corona discharge and grafted by acryl amide a linear dependence on the current density was found (Lei et al., 2000). At the same time, after the grafting a decrease of concentration of hydroperoxides exhibited the result of linking of acryl amide on the active centers of modified iPP. In the case of modification of PO a time factor negatively affects the adhesion properties. The efficiency of modification decreases with the time elapsed from modification. For the given reasons a condition for the formation of strong adhesive bonds is an immediate processing of iPP after the modification.

### 3.1.1 Modification of iPP by corona discharge

One of the most effective methods of modification of iPP is its surface modification using electric discharge plasma at the atmospheric pressure (corona discharge) (Sun et al., 1999; Strobel et al., 2003). 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 surface energy and polarity increase. In our experiments (Novák & Chodák, 1998), summarized in Figs. 1 – 8, the surface properties of iPP modified by corona discharge at varying parameters, e.g. current density, exposition time, aging, have been studied and the influence of polymer crystallinity on the surface properties has been investigated, too.

The dependence of the surface energy of the iPP modified by corona discharge on current density is represented in Fig. 1. After an initial induction period (up to 0.4 mA) a more rapid increase in surface energy was observed. As seen in Fig. 1, the increase in surface energy is by 3 - 5 mJ.m<sup>-2</sup> higher for the extruded iPP compared to the biaxially oriented polymer. According to Fig. 1, an increase of the surface energy was observed for biaxially oriented iPP (curve b) from 30 to 39 mJ.m<sup>-2</sup>, while for extruded iPP (curve a) surface energy value was found to be 49 mJ.m<sup>-2</sup>. At higher current densities ( $I > 0.6$  mA) the difference between the surface energy values of modified extruded and biaxially oriented iPP was enhanced from 3 to 10 mJ.m<sup>-2</sup>. Retardation was observed for biaxially oriented iPP above the current density of 0.6 mA. On the other hand, no retardation occurred for the extruded iPP with lower crystallinity. The observed phenomena can be explained by some kind of saturation of the surface of biaxially oriented iPP by degradation products formed during modification.

The difference in the values of the surface energy between two corona discharge modified iPP results from the different degree of crystallinity. A higher degree of crystallinity of biaxially oriented iPP prevents surface oxidation. The oxidation takes place in amorphous phase and at defect spots, which are expected to be more frequent on the surface of extruded foil when compared with the surface of the biaxially oriented iPP foil.

The dependence of the total surface energy of biaxially oriented iPP as well as its dispersive component on current density is shown in Fig. 2. The surface energy of non-modified biaxially oriented iPP is very low and consists mainly of the dispersive component. These results reflect poor adhesive properties of non-modified iPP. A substantial rise of the surface energy was observed after an initial induction period (Fig. 2, curves a, b). A more intensive retardation was observed for dispersive component of the surface energy (plot b) at the current density above 0.6 mA. On the other hand, lower retardation occurred for the total surface energy (plot a). The explanation of observed dependences in Fig. 2 is similar to that for dependences in previous Fig. 1, i.e. the saturation of polymer surface by degradation products formed during the modification. The values of dispersive part of the surface energy are stabilized.

The dependence of PC of the surface energy on the current density is shown in Fig. 3 for biaxially oriented iPP modified by corona discharge. The PC of the surface energy for unmodified biaxially oriented iPP is low ( $0.4 \text{ mJ.m}^{-2}$ ). Modification by corona discharge results in a significant increase of the PC of the surface energy. The increase in current density leads to a linear rise of the PC of the surface energy. The value  $5 \text{ mJ.m}^{-2}$  was reached at  $I = 0.8 \text{ A}$  representing 12.8 % of the value of the surface energy.

The dependence of the surface energy of iPP modified by corona discharge on exposure time defined by a speed of the foil drive is represented in Fig. 4. The increase in surface energy of both iPP is much less pronounced at higher speed of foil drive, which is inversely proportional to the exposure time of corona discharge modification. According to the Fig. 4, extruded iPP is more sensitive to the changes of speed of foil drive than biaxially oriented foil since the increase in the speed of foil drive from  $4.8$  to  $90 \text{ m.min}^{-1}$  leads to a decrease of the surface energy for extruded iPP from  $49$  to  $25 \text{ mJ.m}^{-2}$  while for biaxially oriented iPP the values change from  $39$  to  $32.5 \text{ mJ.m}^{-2}$ .

The concentration of hydroperoxides in the biaxially oriented iPP modified by corona discharge increased linearly with current density (Fig. 5). If the current density rises by  $0.5 \text{ mA}$ , the concentration of hydroperoxides increased by a factor 2.9. A determination of hydroperoxides groups amount as a function of corona discharge current density allows estimating the iPP hydrophilicity according to the concentration of polar groups. The dependence in Fig. 5 is in agreement with the dependence of PC of the surface energy shown in Fig. 3. From the comparison of these two dependences a linear dependence of PC of the surface energy with hydroperoxide concentration can be expected.

If the time of exposure to corona discharge of the sample of biaxially oriented iPP is shortened, the concentration of hydroperoxides decreases (Fig. 6). The effect of the increase in the speed of the foil movement at continuous modification of PP by a corona treatment is similar to the decrease of current density. The dependences in Fig. 6 are nonlinear and demonstrate the reciprocal relation between the effect of speed of foil movement, i.e. the time of corona treatment, and current density. According to Fig. 6 the hydroperoxide concentration was the same if the speed was  $90 \text{ m.min}^{-1}$  and  $I = 0.8 \text{ mA}$  or if the foil moved

4.8 m.min<sup>-1</sup> at I = 0.3 mA. If the speed of foil drive rises from 40 m.min<sup>-1</sup> up to 80 m.min<sup>-1</sup>, the concentration of hydroperoxide is only about 6 % of the value for lower speed.

The most serious problem preventing wide application of corona discharge modification of polymers is the durability of the effect, i.e. a rapid decrease of wettability during hydrophobic recovery. One explanation of the deterioration in surface properties of modified iPP has been considered to be migration of the created polar moieties into the polymer bulk. Another explanation is based on a decomposition of polar groups formed during aging. Because of hydrophobic recovery the surface energy of extruded iPP rapidly decreases during the first 24 hours (Fig. 7, plot a), then the decrease slows down and after 240 hours it levels off. Different behaviour was observed for the biaxially oriented iPP (Fig. 7, plot b). The surface energy in this case did not change significantly during storing. The value of the surface energy of biaxially oriented iPP is almost identical with the corresponding value for the foil of extruded iPP stored for a long time.

The modified layer on iPP surface consisting from macromolecules with many oxidizing groups contributes to the self-adhesive properties of iPP. The weak cohesion of this, only several micrometers thick layer, causes the adhesive joints to be less mechanically resistant. The stability of hydroperoxides at the surface was investigated by measuring the strength of auto adhesive joints (Fig. 8). At the contact of two surfaces of modified iPP foils new bonding may arise between these surfaces because of hydroperoxide decomposition. The data in Fig. 8 indicate that the work of auto adhesion increases with temperature of the formation of auto adhesive joints. This fact corresponds well with the decrease of the concentration of hydroperoxides determined after destruction of auto-adhesive joints. The concentration of hydroperoxides is almost zero at 423 K.

The practical aspect of the iPP surface modification by the corona discharge can be demonstrated on the adhesive properties of modified and unmodified iPP carpet fabrics treated by rubbing pastes based on butyl acrylate-vinyl acetate copolymer. The results are summarized in Table 1. According to Table 1 the value of mechanical work of adhesion towards PP is rising with the increase of the rubbing paste mass.

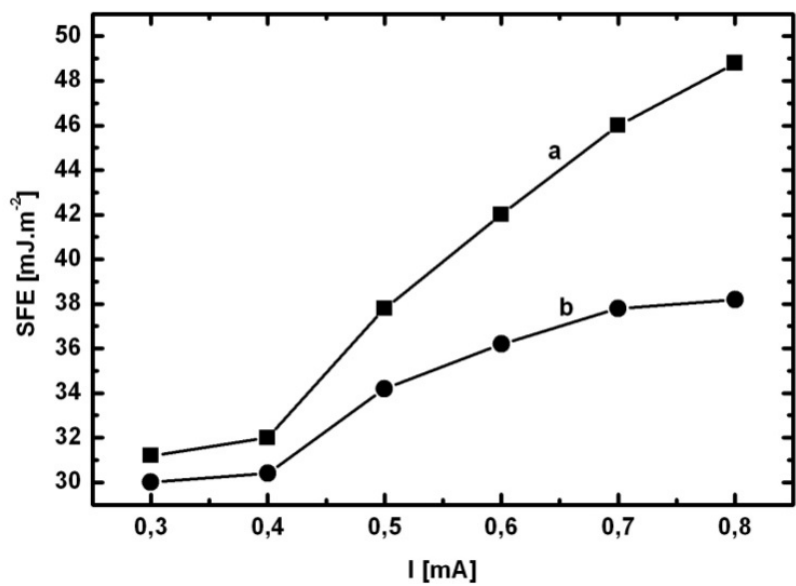


Fig. 1. Surface energy of iPP modified by corona discharge ( $v = 4.8 \text{ m.min}^{-1}$ ) as a function of current density: a - extruded iPP, b - biaxially oriented iPP

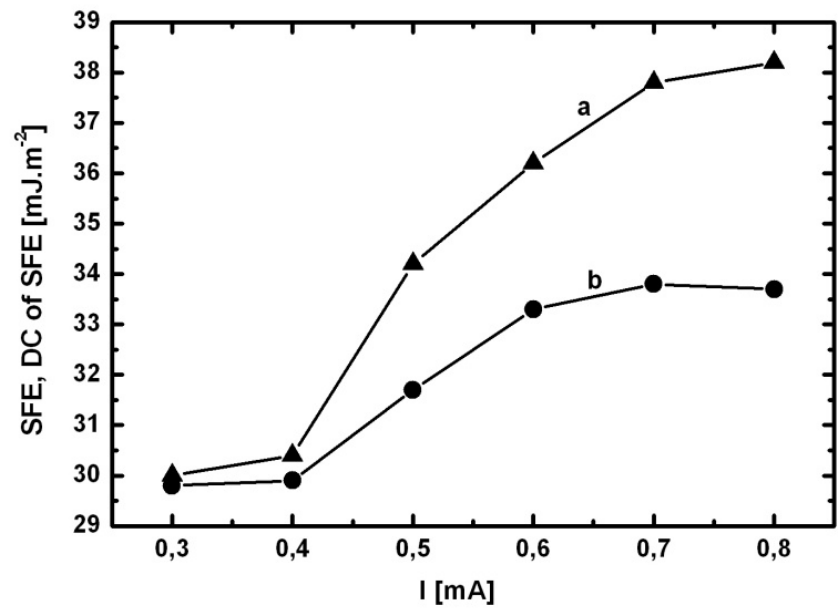


Fig. 2. Surface energy and its dispersive component as a function of current density for the biaxially oriented iPP modified ( $v = 4.8 \text{ m.min}^{-1}$ ) by corona discharge: a - surface energy, b - dispersive component of the surface energy

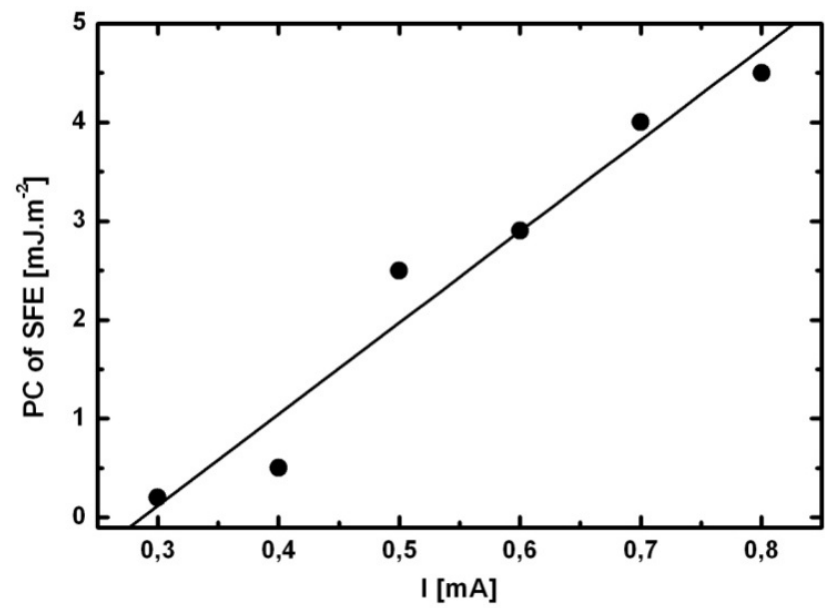


Fig. 3. PC of the surface energy as a function of current density for the biaxially oriented iPP modified ( $v = 4.8 \text{ m.min}^{-1}$ ) by corona discharge



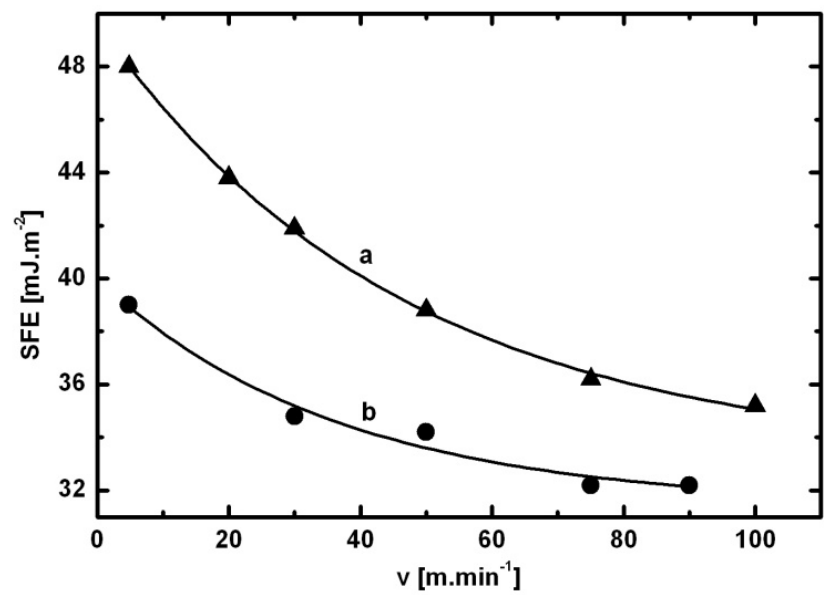


Fig. 4. Surface energy of iPP modified by corona discharge as a function of foil drive ( $I = 0.8$  mA); a - extruded iPP, b - biaxially oriented iPP.

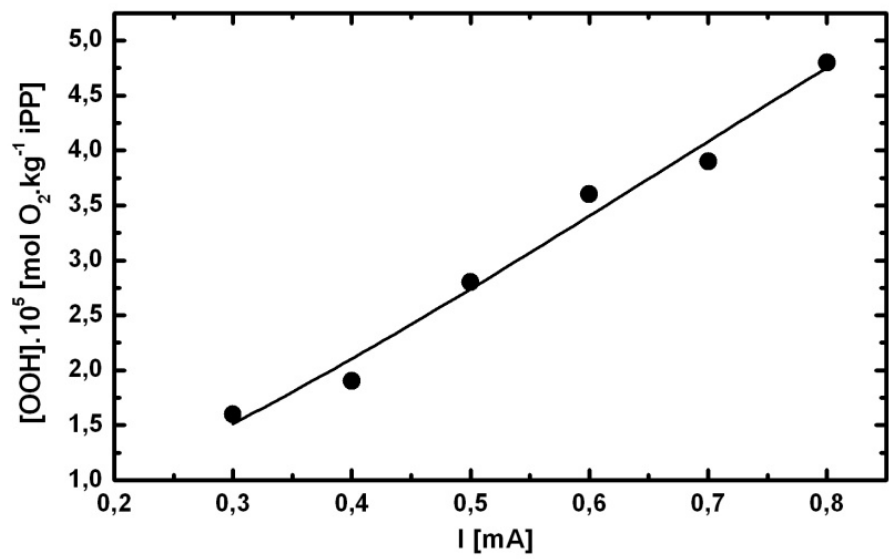


Fig. 5. Concentration of hydroperoxides in the biaxially oriented iPP modifiedby corona discharge as a function of current density ( $v = 4.8$  m.min<sup>-1</sup>)

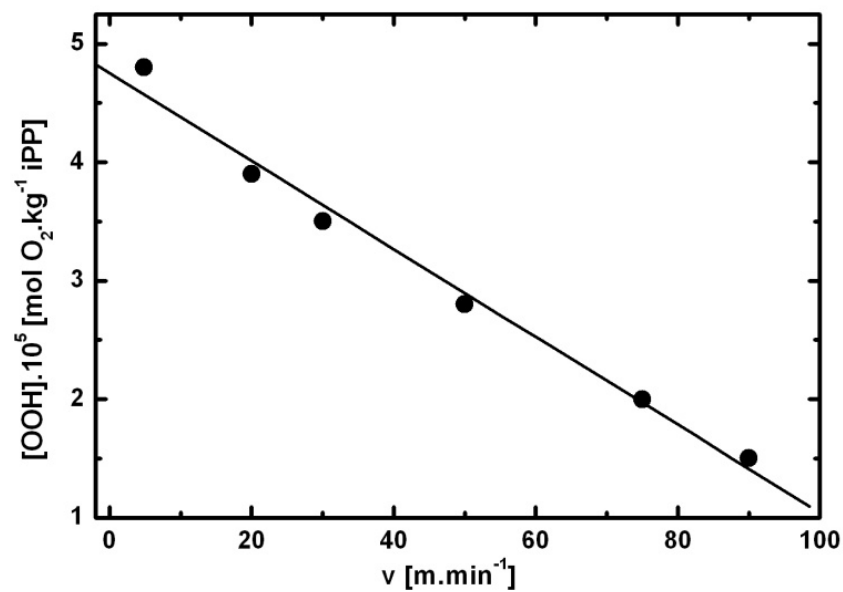


Fig. 6. Concentration of hydroperoxides in the biaxially oriented iPP modified by corona discharge as a function of foil drive speed ( $I = 0.8 \text{ mA}$ )

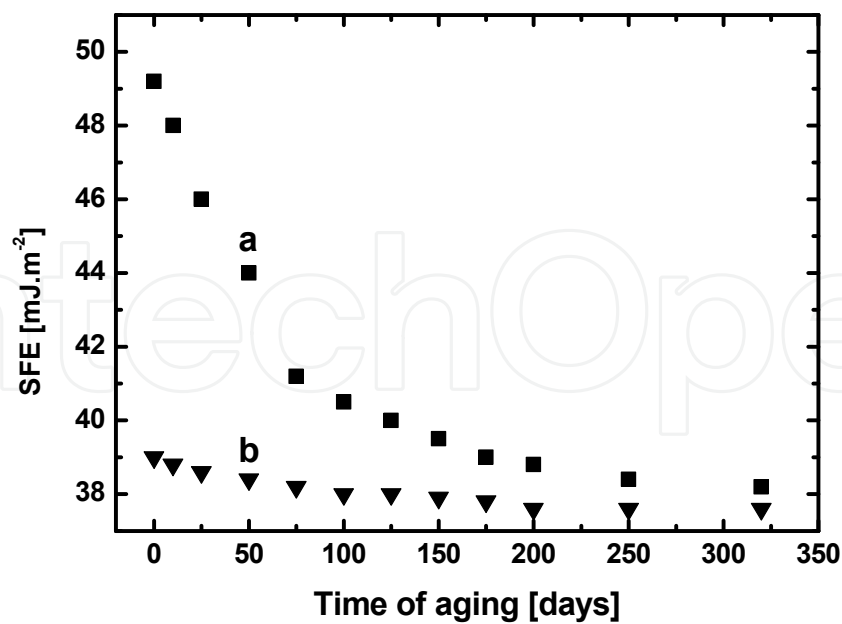


Fig. 7. Variation of the surface energy of iPP modified by corona discharge with time of aging: a - extruded PP, b - biaxially oriented PP

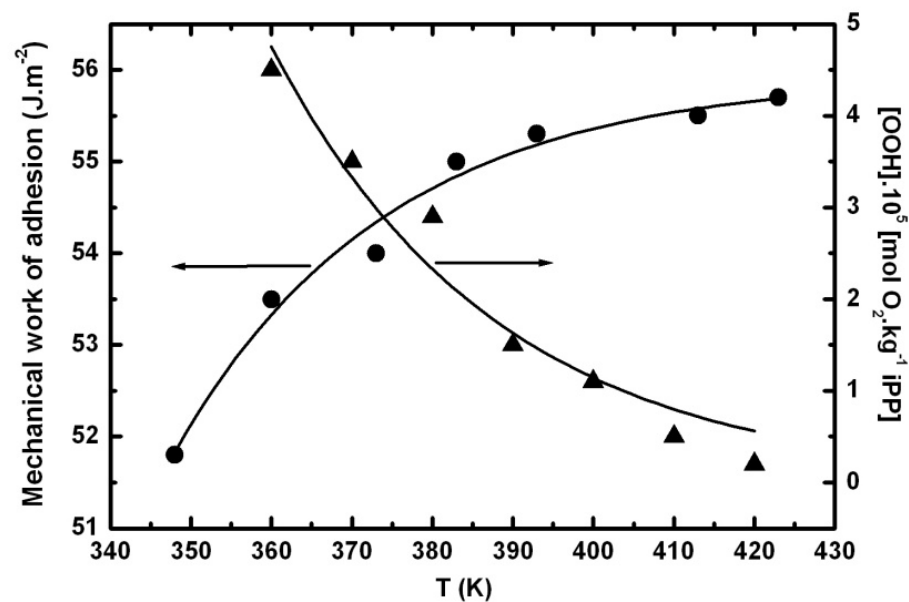


Fig. 8. Variation of auto-adhesion work and hydroperoxide concentration of iPP modified by corona discharge with the time of auto-adhesive joint formation

	Deposit of butyl acrylate-vinyl acetate copolymer ( g.m <sup>-2</sup> )			
	50	100	130	150
	Am ( J.m <sup>-2</sup> )			
Unmodified tissue	42	50	59	69
Modified tissue	78	84	94	102

Table 1. Mechanical work of adhesion in the adhesive joint iPP backing fabric-butyl acrylate-vinyl acetate copolymer deposit

Modification is the most important factor, since with 50 g.cm<sup>-2</sup> of the rubbing paste on iPP fabric the mechanical work of adhesion was higher than that for unmodified PP fabric with 150 g.cm<sup>-2</sup> layer of the rubbing paste. The adhesive properties given as the values of the work of adhesion improved, on average, by 65 % when compared the backing fabric based on modified PP fabrics non-modified material.

The higher efficiency of the modification for extruded iPP when compared to biaxially oriented iPP was explained by different susceptibility to oxidation due to different crystallinity. Linear dependence of either PC of the surface energy or hydroperoxide concentration of modified iPP on current density was observed. A decrease in the exposition time of iPP foil resulted in lower modification effect. The sensitivity on exposition time was more pronounced for extruded iPP. Aging of modified PP foil leads to a significant drop in surface energy during first 24 hours for extruded iPP, while for biaxially oriented iPP the decrease was small. An increase of the mechanical work of adhesion was observed if temperature of auto-adhesive joints rised. The observed decrease of hydroperoxide concentration after a destruction of the auto-adhesive joints is in accordance with the previous data.

The insufficient stability of the polarity of such a polymer surface after modification by the corona discharge brings some difficulties, i.e. due to the fact that some instable oxygenic functional groups such as peroxide or hydroperoxide groups are formed and subsequently decompose to give the more stable ketone and aldehyde groups. Because of thermodynamic preference, the surface energy of the polymer decreases due to the transfer of polar functional groups from the surface of polymer into the bulk. 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 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 corona discharge plasma and to take into account this fact before further processing of the stored modified iPP films.

Variation of the surface energy and its PC with time after modification is represented in Fig. 9 for biaxially oriented iPP modified by corona discharge. During aging the hydrophilicity of the modified biaxially oriented iPP films initially dropped. The decrease in hydrophilicity (Fig. 9) manifested itself by a non-linear fall in surface energy (plot a) as well as PC of the surface energy (plot b) while the greatest fall in surface energy and its PC was found after 30 days following modification when the value of the surface energy had fallen from 39.2 to 37.0 mJm<sup>-2</sup>. A greater relative decrease was observed for PC of the surface energy, which fell from 9.2 to 6.8 mJ.m<sup>-2</sup> during 30 days after modification. In the course of further aging the process of iPP hydrophobization proceeds rather slow and after 360 days the surface energy and its PC reached 35.7 mJ.m<sup>-2</sup> and 5.5 mJ.m<sup>-2</sup>, respectively. From these values, one year after modification of the biaxially oriented iPP by the electric discharge the total surface energy decreased only a little - 9%, while the PC of the surface energy fell up to 40% when compared with that of a fresh modified sample. The measurements of the surface energy and its PC biaxially oriented iPP modified by the corona discharge show an increase of investigated surface parameters while the dispersive component of the surface energy remained practically unchanged.

Dependencies of the surface energy and its PC against long-term aging are represented in Fig.10 for extruded iPP modified by corona discharge (Novák & Florián, 2001; Novák & Florián, 2004). In comparison with biaxially oriented iPP the hydrophobic recovery of extruded iPP films subjected to modification by the electric discharge was much more obvious and the total surface energy (plot a) and its PC (plot b) fell especially in the course of the first 30 days after modification in the same manner as observed for biaxially oriented iPP. According to Fig. 10 the decrease in the hydrophilicity of extruded iPP manifested itself by a non-linear decrease in the surface energy and the PC of the surface energy. While the value of the total surface energy dropped significantly from 46 to 35 mJ.m<sup>-2</sup>, the PC of the surface energy declined still more in this interval, i.e. from 15.8 to 4.6 mJ.m<sup>-2</sup>. 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 surface energy and its PC attained 33.4 mJ.m<sup>-2</sup> and 3 mJ.m<sup>-2</sup>, respectively. On this basis we can state that the total surface energy of the modified extruded iPP decreased by 24% after 30 days and 27% after 360 days following modification. On the other hand, the PC of the surface energy 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 surface energy and its PC obtained for the biaxially oriented iPP and the extruded iPP

modified by the corona discharge, we can conclude that the extruded iPP exhibits essentially higher dynamics for the hydrophobic recovery process than biaxially oriented iPP does (compare Fig. 9 a and Fig. 10). This difference is to be attributed to the different crystallinity of extruded and biaxially oriented iPP. The modification of iPP due to linking polar functional groups to the polymer chain takes place in the amorphous phase of the polymer. This is more significant in the case of extruded iPP, which has lower crystallinity when compared with biaxially oriented iPP. Owing to this lower crystallinity of modified extruded iPP a higher polymer polarity and thus a higher value of its surface energy results. Fig. 11 depicts the polar fraction for biaxially oriented iPP (plot a) and for extruded iPP (plot b) after modification by the electric discharge in the process of long-term hydrophobic recovery.

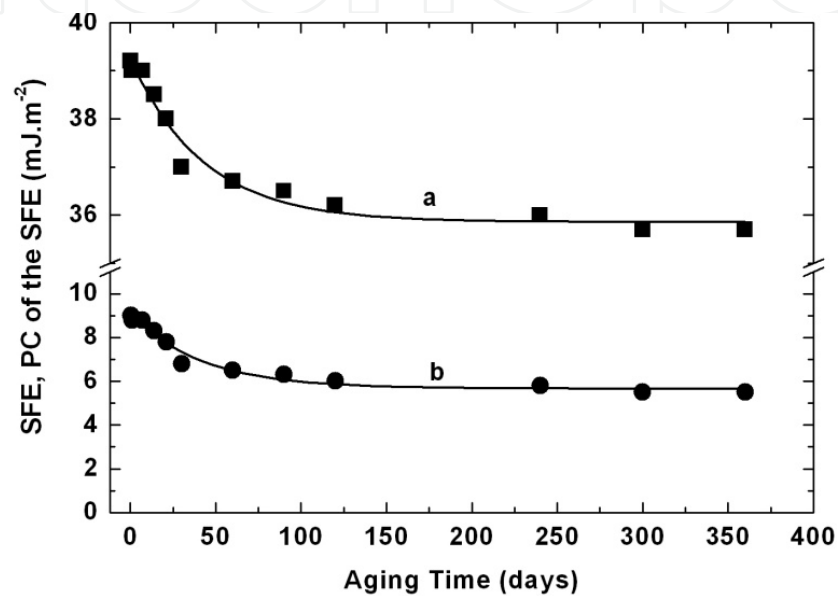


Fig. 9. Surface energy and its PC of biaxially oriented iPP modified by corona discharge during long-term hydrophobic recovery: a – surface energy, b – PC of the SFE

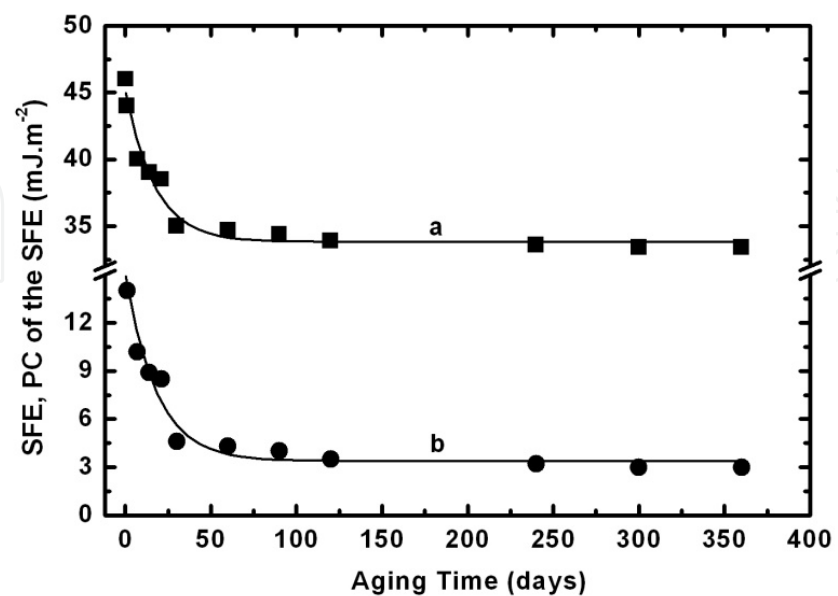


Fig. 10. Surface energy and its PC of extruded iPP modified by corona discharge during long-term hydrophobic recovery: a – surface energy, b – PC of the SFE

According to Fig.11 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 biaxially oriented polymer, 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 electric discharge was observed over 30 days after modification and during further aging the decrease was rather less for both extruded and biaxially oriented iPP. If we compare plot a with plot b in Fig.11, 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 twofold when compared with that of biaxially oriented iPP.

Fig.12 presents the dependence of the mechanical work of adhesion of iPP modified by the electric discharge for an adhesive joint with polyvinyl acetate on aging the modified biaxially oriented iPP (plot a) and extruded iPP (plot b). In the course of aging of the iPP films the mechanical work of adhesion to polyvinyl acetate fell in a non-linear manner. After 360 days of aging the mechanical work of adhesion fell 26 % for modified biaxially oriented iPP when compared with original value of the mechanical work of adhesion and by 52 % for modified extruded iPP. As for the polar fraction the greatest decrease in mechanical work of adhesion to polyvinyl acetate produced by hydrophobic recovery of the surface of modified iPP was observed after 30 days following modification. During further aging a significant decrease in mechanical work of adhesion was also observed.

Because of the apparent correlation between mechanical work of adhesion and the polar fraction found for iPP modified by the electric discharge we have constructed the relationship between mechanical work of adhesion and polar fraction given in Fig. 13. The polar fraction faithfully expresses the change in polarity of the modified iPP during long-term aging. Thus Fig. 13 gives the change in mechanical work of adhesion in the course of long-term hydrophobic recovery of the surface of the modified iPP. The discussed relationship exhibits linear character and can be described by the equation:

$$A_m = 65.9 + 3.9 \cdot 10^2 \cdot x_s^p, r^2 = 0.99 \quad (20)$$

Because of the value of correlation coefficient found we can state that the linearity of the relationship given in Fig. 13 has been confirmed for the long-term aging of iPP after modification.

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. 14 for biaxially oriented iPP (plot a) and extruded iPP (plot b) modified by the electric discharge. According to Fig. 14 the decrease in adhesive properties is significantly smaller for biaxially oriented iPP when compared with that of the extruded iPP in contradiction with assumptions based on the values found of the PC of the SFE. The decrease in values of the PC of the surface energy, the polar fraction and the mechanical work of adhesion for iPP modified by electric discharge may 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 surface energy because of the thermodynamic preferences present and thus to



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

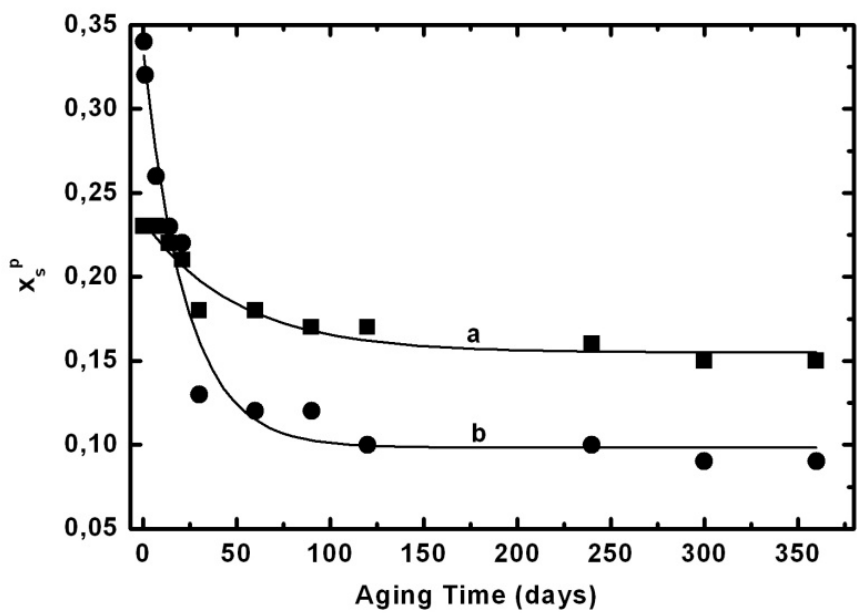


Fig. 11. Polar fraction of the iPP surface modified by corona discharge during long-term hydrophobic recovery: a – biaxially oriented iPP, b – extruded iPP

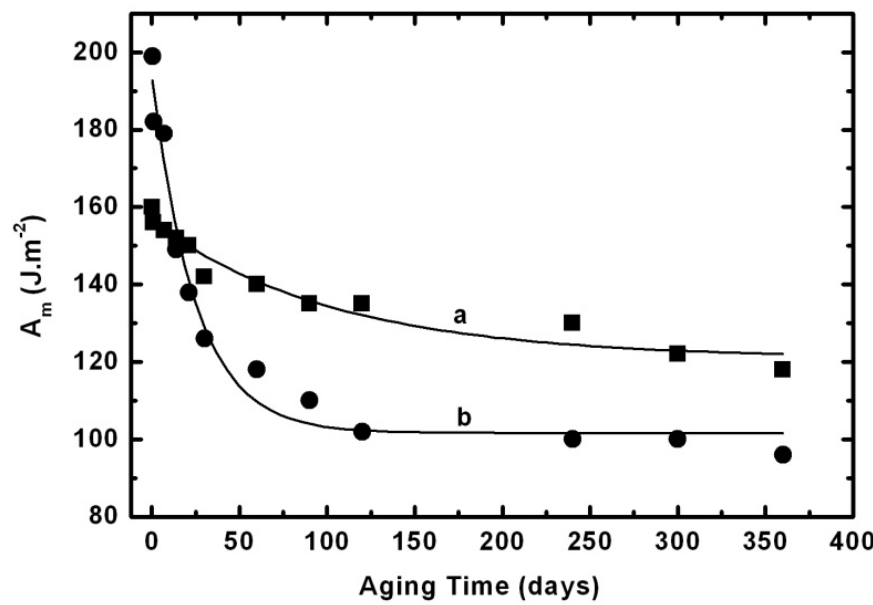


Fig. 12. Mechanical work of adhesion to polyvinyl acetate for iPP modified by corona discharge during long-term aging: a – biaxially oriented iPP, b – extruded iPP

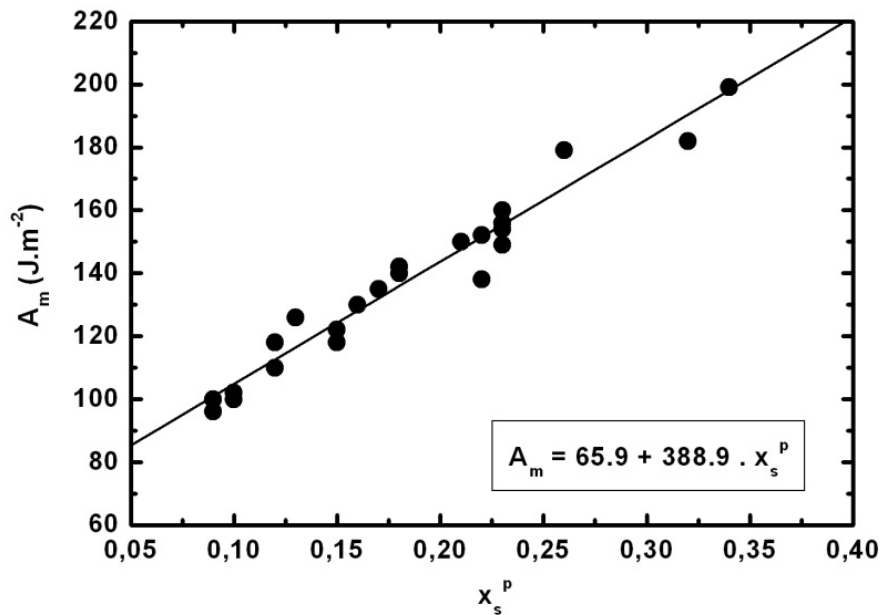


Fig. 13. Dependence of the mechanical work of adhesion to polyvinyl acetate for iPP modified by corona discharge plasma vs. polar fraction

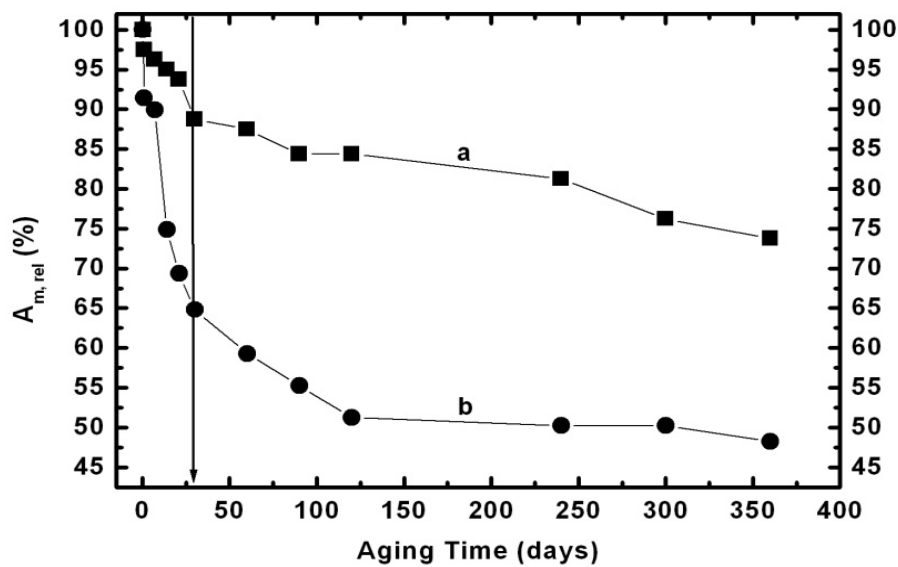


Fig. 14. Variation of the relative change in the strength of the adhesive joint modified iPP – polyvinyl acetate during long-term hydrophobic recovery: a – biaxially oriented, b – extruded iPP.

3.2 Modification by grafting

Grafting of some polar polymers (Rätzsch et al., 2002; Castell et al., 2004; Kuhn et al., 2000; Scarlatti et al., 2004; Shi et al., 2001; Pesetskii et al., 2001; Kato et al., 2003; Sulek et al., 2001; Tao et al., 2001; Flores-Gallardo et al., 2001; Yamada et al., 2003), such as acryl amide, maleic anhydride, methyl methacrylate, itaconic acid (IA) onto iPP chain, is a possibility for the increase of both the surface polarity and hydrophilicity of iPP. The free-radical

polymerization methods are most widely used and inexpensive procedures for the synthesis of graft copolymers of iPP because they are relatively simple. This is a common method of increasing of iPP adhesive properties. The main chain and the branch chains in grafted iPP are usually thermodynamically incompatible. Grafting improves adhesion, dyeing, tensile strength, compatibility, thermal stability and abrasion resistance of the copolymer.

The results of surface characteristics of iPP grafted by IA (Novák & Florián, 1995; Novák & Chodák, 1995) are shown in Fig. 15. As seen in Fig. 15, plot a, the surface energy of iPP grows with the increase of concentration of grafted IA. The grafting of 5 wt. % of IA onto iPP macromolecule increased the surface energy by 19.5 % in comparison with unmodified iPP. This increase should be attributed mainly to the growth of PC of the surface energy (Fig. 15, plot b). The PC of the surface energy increased after grafting of iPP by 5 wt.% from the value 0.4 mJ.m<sup>-2</sup> (non-modified polymer) to 9.5 mJ.m<sup>-2</sup> obtained for iPP containing 5 wt.% of grafted IA.

The results in Fig. 16 show that the adhesion of iPP to more polar polymers as well as to metals (Fig. 17) is low. The difference between a polarity of iPP and other more polar polymer as a consequence of iPP grafting by IA was diminished. The adhesion parameters in the system iPP grafted by IA - more polar polymer increases with an increase of the IA grafted content. Grafting of iPP by 5 wt.% of IA leads to a growth of mechanical work of adhesion of iPP 6.9 times, 7.2 times and 18.1 times when considering the adhesion of iPP to cellulose acetate, polyamide and aluminum, respectively.

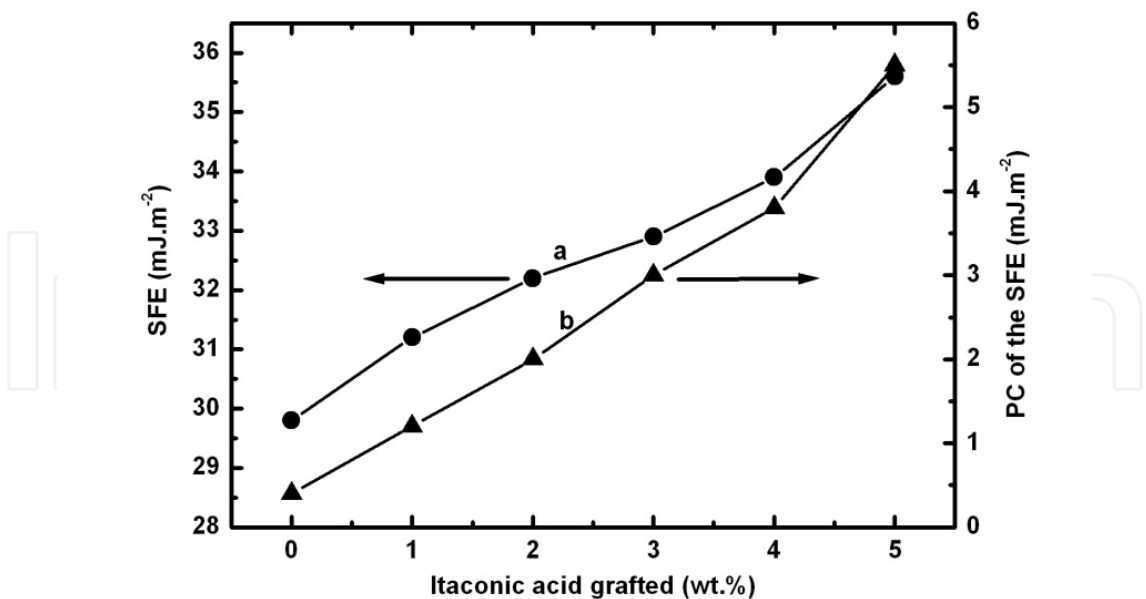


Fig. 15. Surface energy and its PC of iPP grafted by itaconic acid against itaconic acid grafted content

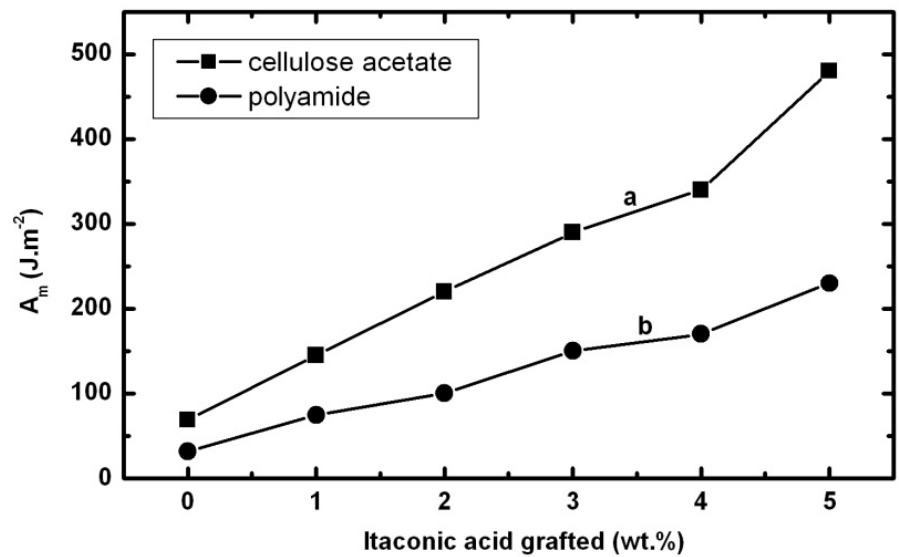


Fig. 16. Mechanical work of adhesion of iPP grafted by itaconic acid to cellulose acetate (a) and polyamide (b) against itaconic acid grafted concentration

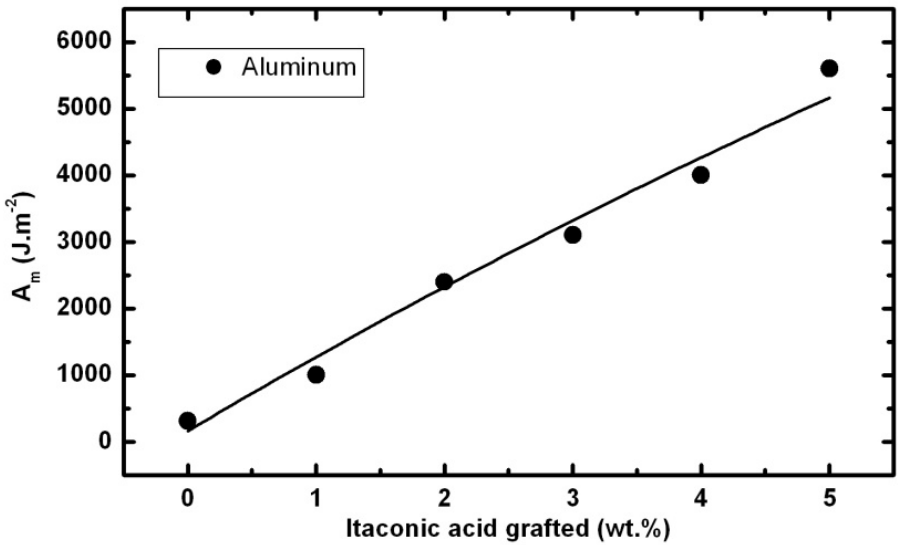


Fig. 17. Mechanical work of adhesion of iPP grafted by itaconic acid to aluminum against itaconic acid grafted concentration

3.3 Modification by oxidation

The significant groups of adhesive properties of iPP increasing present oxidation methods (Brewis & Mathieson, 2002; Chodák & Novák, 1999; Ashana et al., 1997; Novák, 1996; Yang et al., 2003; Nie et al., 2000; Novák & Pollák, 1994; Novák, 1996; Dibyendu et al.,1998; Vasconcellos et al.,1997; Novák & Chodák, 2001). As a result of formation of carbonyl groups in the course of iPP modification the adhesive properties of polymers are increased. Using a strong oxidation agent and higher temperatures of modification a partial decomposition of the polymer can occur when the bulk unmodified zones of polymer reach the surface. On spherulitic surfaces of iPP chromic acid preferentially etches the less

ordered (amorphous) regions between the arms of spherulites, producing ca 10  $\mu\text{m}$  deep cavities. On lamellar surfaces, chromo sulfuric acid preferentially attacks interlamellar regions, producing deep cavities. The deeply etched spherulitic and lamellar surfaces have numerous mechanical anchoring sites for metal to adhere strongly. For the increase of adhesion of iPP functional groups  $=\text{C}=\text{O}$  and  $-\text{SO}_3\text{H}$  are responsible, which are formed during the modification and are present in the near-surface layer. In iPP modified by chromo sulfuric acid there is also a high concentration of carboxyl groups. After the modification of iPP by chromo sulfuric acid a very rough surface is formed and that the roughness itself can cause a good adhesion of treated iPP. A different opinion on the better adhesion properties after modification by chromo sulfuric mixture considers a main reason for the better adhesion properties to be the higher polarity of pre-treated iPP, while the higher roughness to be a secondary importance contributing the higher adhesion only. For the modified iPP similar correlations were found between the degree of oxidation or concentration of carboxyl group and adhesion. From the results of the studies on the surface energy of iPP modified by chromo sulfuric acid it follows that after initial fast increase, during 1 - 2 minutes of modification, the value of the surface energy levels off. The most suitable temperature for modification of iPP by chromo sulfuric acid is 70  $^{\circ}\text{C}$ , at which the degradation of polymer is still not extensive. In the measurement of mechanical work of adhesion of iPP modified by chromo sulfuric acid in a joint with polyvinyl acetate the result was six times larger relatively to the untreated iPP. This result is similar to that for the modification by corona discharge besides the fact that the modification by chromo sulfuric acid has a lasting character.

An efficient method of modification of iPP from the point of view of enhancement of adhesion properties is a modification by vapors of chromyl chloride (Novák, 1996; Novák & Pollák, 1994). In contrast to the modification by chromo sulfuric acid a considerably longer time of modification is needed (40 - 60 min.) and the treatment is performed in the temperature range of 30 - 60  $^{\circ}\text{C}$ . The study shows few times higher concentration of carbonyl groups in comparison to treatment by chromo sulfuric acid, while  $\text{Cr}^{\text{VI}}$  was reduced to lower oxidation degrees up to  $\text{Cr}^{\text{IV}}$ . In the study of a dependence of PC of the surface energy on time of modification a maximum was observed and it was confirmed at the same conditions also for the similar dependence of concentration  $\text{Cr}^{\text{IV}}$  by ESR method. In the course of modification of iPP by chromyl chloride at higher degrees of oxidation a degradation of iPP (linear decrease of molar mass with the time of modification) was observed. The modification mechanism of chemical etching by oxidizing agents consists in the abstraction of the hydrogen atoms from the polymer backbone and their replacement with polar groups. These polar groups introduced on the iPP surface by pretreatment should increase the surface energy and enhance the wetting. The surface pretreatment by some oxidizers has also another aim - to remove all weak boundary layers on the polymer surface e.g. stabilizers and other additives, which are responding for the weak adhesive bonds. The oxidizing chemical methods of iPP modification are efficient and in addition to this fact they give a more durable result than modification by corona discharge.

The results of the investigation of surface properties of iPP pretreated by chromyl chloride and/or chromo sulfuric acid are presented in Figs. 18 - 26.

Variation of the surface energy of iPP modified by chromyl chloride with modification time is represented in Fig. 18. It follows that the surface energy non-linearly increases with modification time. However, it becomes stable after a certain period of time. The lower the temperature of modification, the later the stable state appears. For instance, the stable state of the relationship described in Fig. 18 appeared after 30 minutes if the modification was performed at 333 K and after 60 minutes if the modification was performed at 303 K. The stabilization of the values of the surface energy and the shift towards longer time due to the decrease in the temperature of oxidation (Fig. 18) can be explained by stepwise saturation of the polymer surface with polar (mainly carbonyl) groups, which originate from modification of iPP by chromyl chloride. The increase in surface energy of iPP modified by chromyl chloride (Fig. 18, plots a, b, c) was 36 % for the temperature of 333 K, 28 % for 313 K and 13 % for 303 K with respect to non-modified polymer.

The dependence of the surface energy and its PC against time of oxidation is represented in Fig. 19 for iPP modified by chromyl chloride. According to Fig. 19, the PC of the surface energy of modified iPP increases during the first 30 - 40 min. of modification, after this period the value of PC decreases. The reaching the maximum of PC of the surface energy may be probably ascribed to degradation processes occurring at the modified polymeric surface, which could decrease the polarity of the surface. After a certain period of time the degradation products accumulate at the surface of iPP reducing the polarity, which brings a decrease in surface energy of polymer.

In iPP modified by chromyl chloride the concentration of carbonyl groups was determined (Fig. 20). The concentration of the carbonyl groups increased with the time of oxidation and reaches a constant value after 30 - 60 min., depending on the temperature of modification. Plots a, b, c in Fig. 20 correspond to the temperatures 333 K, 313 K and 303 K, respectively, exhibit analogous course like the plots of the surface energy in Fig. 24. Change the temperature of modification from 303 to 333 K, the concentration of the surface carbonyl groups increases by the factor 4.4. Saturation of the surface with carbonyl groups is probably the reason for the stabilization of the carbonyl groups concentration after a given time.

Determination of the reaction rate constant of iPP oxidation by chromyl chloride showed a strong dependence of the reaction rate on the temperature (Fig. 21). The growth of the temperature from 303 K to 333 K caused an increase of the reaction rate by the factor 1.9.

The results of the Cr<sup>VI</sup> to Cr<sup>IV</sup> reduction in iPP modified by chromyl chloride obtained using electron spin resonance are represented in Fig. 22. It can be seen that the maximum Cr<sup>IV</sup> concentration at 333 K is reached after 40 min. of oxidation. As it can be seen, the maximum concentration of Cr<sup>IV</sup> was reached after 40 minutes of iPP oxidation at the temperature of 333 K and the curves in Fig. 22 and Fig. 20 are in good correlation.

The dependence of the surface energy and its PC vs. concentration of C=O groups is shown in Fig. 23. The PC of the surface energy reaches a maximum at the C=O groups concentration equal to  $1.6 \times 10^{-2}$  mol O<sup>2</sup>.kg<sup>-1</sup> iPP. The following decrease in the C=O groups concentration is probably caused by an increased amount of the degradation products thus resulting in the decrease of the value of the surface energy.

The degree of the iPP degradation during the modification by chromyl chloride was estimated from the determination of its molecular weights. Like it can be seen from Fig. 24,



the molecular weight of iPP decreases linearly with the time of modification, the slope of the curves is increasing with increased temperature. After 60 min. of modification the molecular weight decrease of iPP is about 10 % for  $T = 303\text{ K}$ , 26 % for  $T = 313\text{ K}$  and 42 % for  $T = 333\text{ K}$ , in comparison with the unmodified iPP.

The decrease of the surface energy with time after iPP modification is described in Fig. 25. As it follows from this figure, the iPP surface after modification by chromyl chloride has a relatively good stability. The decrease of the surface energy value 120 hours after finishing modification is close to 7%, while this decrease reaches 30 – 40 % in 24 hours after modification of iPP by corona discharge.

The mechanical work of adhesion of iPP modified by chromyl chloride and chromo sulfuric acid vs. time of modification is illustrated in Fig. 26. It was found that the mechanical work of adhesion is 36 % higher in the case of chromyl chloride compared to the modification with chromo sulfuric acid. The value of mechanical work of adhesion increased rapidly, in a short time (2 min.) reached the maximum value and soon afterwards assumes a constant value.

It has been found that the surface energy of iPP pretreated by chromyl chloride versus modification time rapidly increases and assumes a constant value. Equal character was observed for the relationship between free surface energy and carbonyl group concentration of modified polymer. After a certain time interval subsequent to modification the decrease in surface energy of treated iPP is negligible. A maximum of the relationship between PC of the surface energy and modification time was revealed.

A quite often used method of modification of iPP is the modification by UV light. In analogy to the treatment by the electric discharge the effect of UV light is exhibited in the air by the formation of hydroperoxides which are consequently transformed by photolysis to ketones. It is known that by the decomposition of hydroperoxides, OOH radicals are formed which can lead to formation of ester, carboxyl and lacton groups and thus enhance the adhesion of iPP. A grafting of polar monomers such as N-vinylpyrrolidone or methacrylic acid to iPP modified by UV light can be used. Enhancement of adhesion was observed and could be effectively expressed by a decrease of contact angle of redistilled water on the surface of polymer from 94 deg to 35 – 60 deg. For modification of iPP is very important to know the effect of the intensity and the distance of the UV source from the treated polymeric surface. A very efficient method of adhesion enhancement of iPP is the modification by phosphorus trichloride with participation of the UV light. By the decomposition of phosphorus trichloride active chlorine is formed which reacts with iPP. This is also accompanied at the same time by the oxidation by ozone formed from oxygen in the air. A significant enhancement of adhesion was observed without a considerable decrease of the film transparency.

The inferior adhesive properties of polyolefins result in many serious problems especially if gluing or printing on these materials is considered. 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.

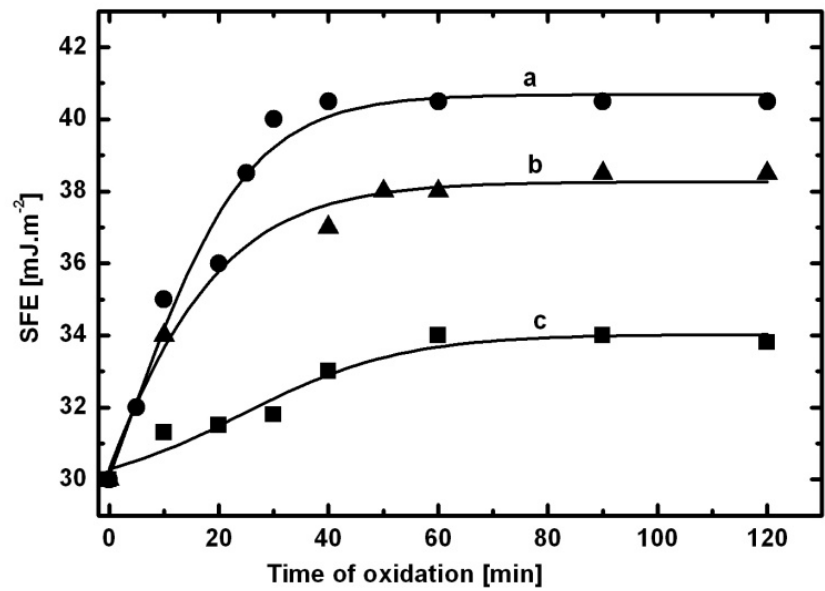


Fig. 18. Surface energy of iPP modified by chromyl chloride against modification time: a -  $T = 333 \text{ K}$ , b -  $T = 313 \text{ K}$ , c -  $T = 303 \text{ K}$

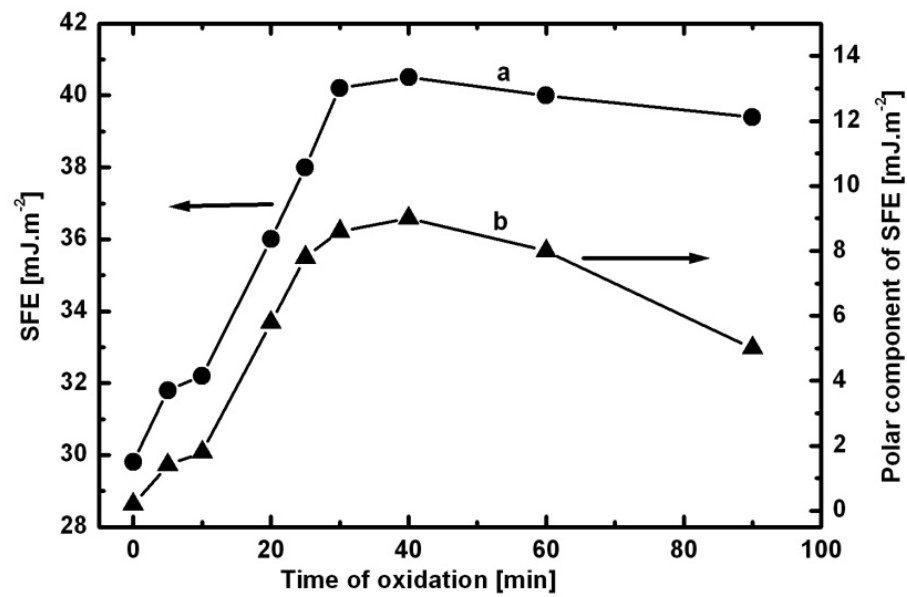


Fig. 19. Surface energy and its PC against time of modification for iPP modified by chromyl chloride: a - surface energy, b - PC of the surface energy.

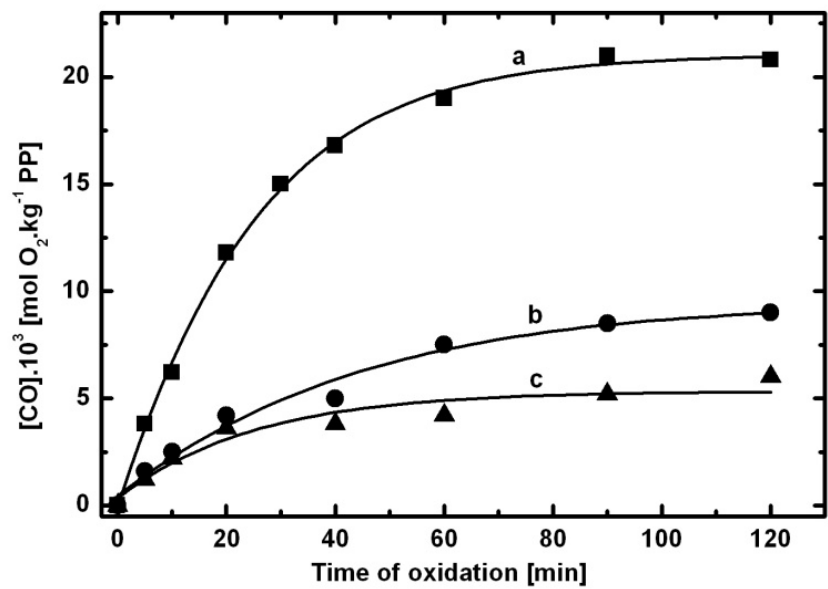


Fig. 20. Concentration of carbonyl groups of iPP modified by chromyl chloride against time of modification: a - T = 333 K, b - T = 313 K, c - T = 303 K

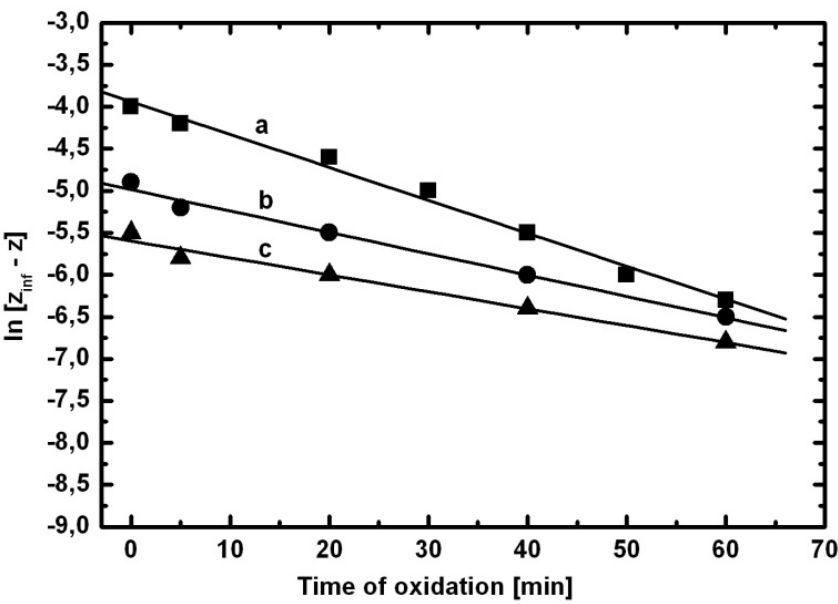


Fig. 21. Determination of the reaction rate constant of iPP modified by chromyl chloride at different temperatures: a – 333 K, b - 313 K, c - 303 K

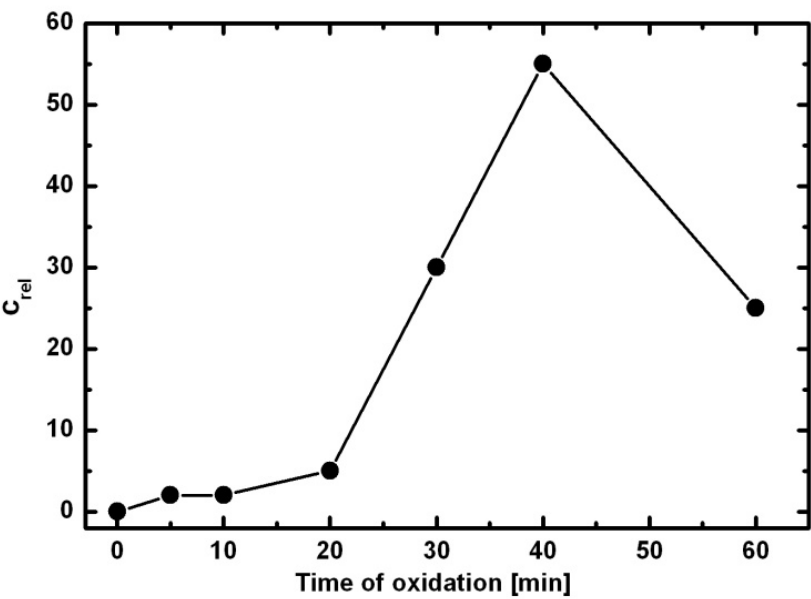


Fig. 22. ESR measurements of Cr<sup>IV</sup> concentration of iPP modified by chromyl chloride against time of modification (T = 333 K)

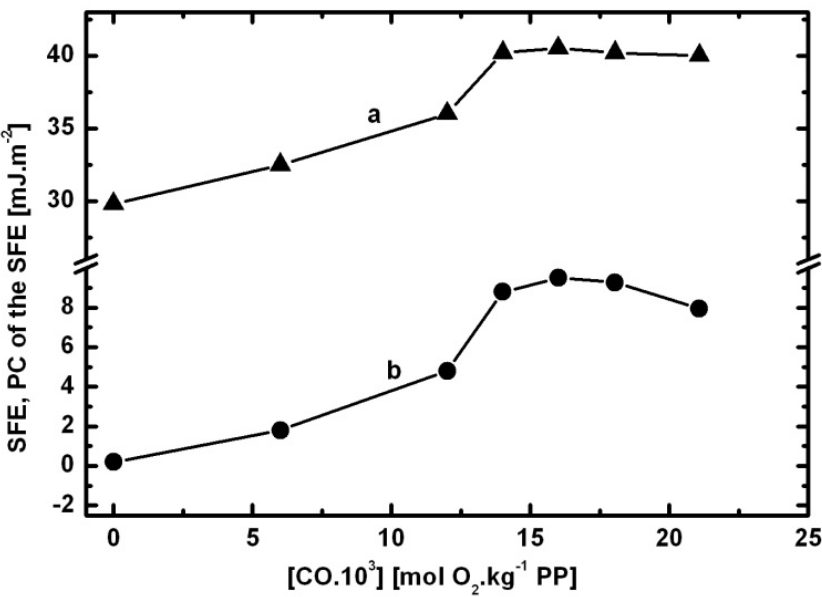


Fig. 23. Surface energy and its PC of iPP modified by chromyl chloride against carbonyl groups concentration: a – surface energy, b – PC of the surface energy

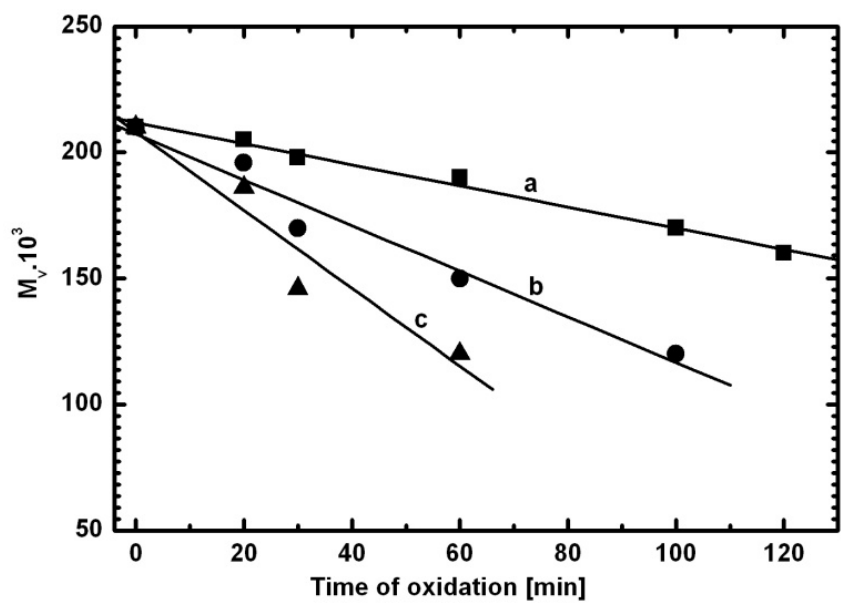


Fig. 24. Figure 24 Molar weight of iPP modified by chromyl chloride vs. time of modification: a -  $T = 303\text{ K}$ , b -  $T = 313\text{ K}$ , c -  $T = 333\text{ K}$

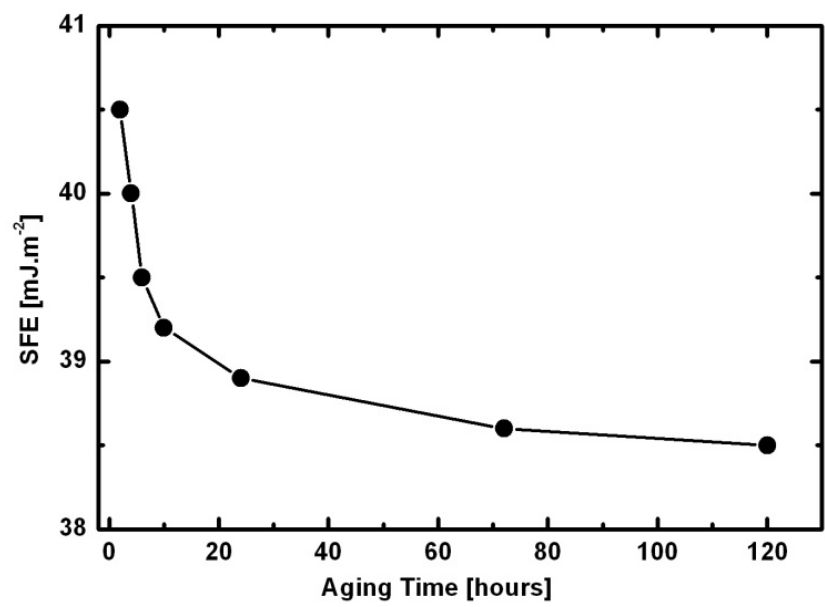


Fig. 25. Surface energy of iPP modified by chromyl chloride vs. time elapsed from modification

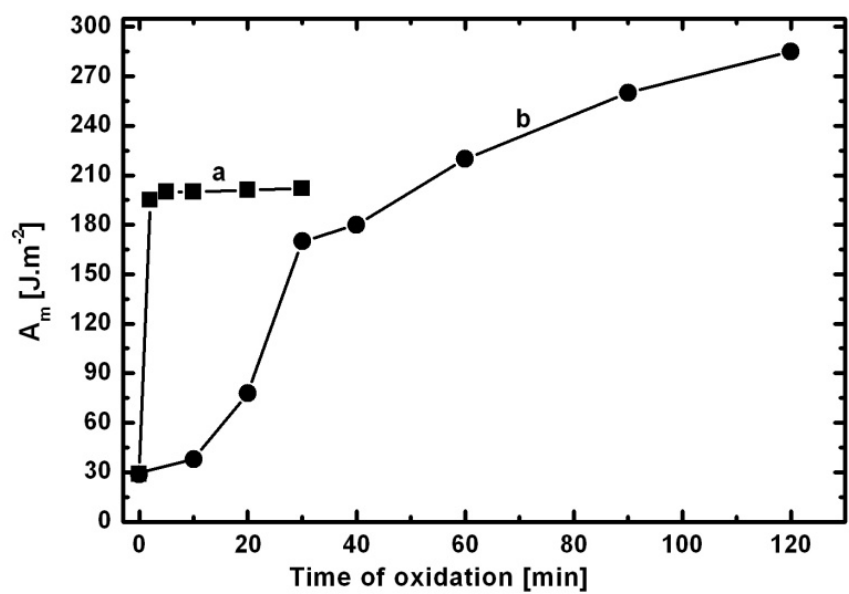


Fig. 26. Mechanical work of adhesion of iPP modified by chromyl chloride to polyvinyl acetate against time of modification: a - chromo sulfuric acid, b - chromyl chloride

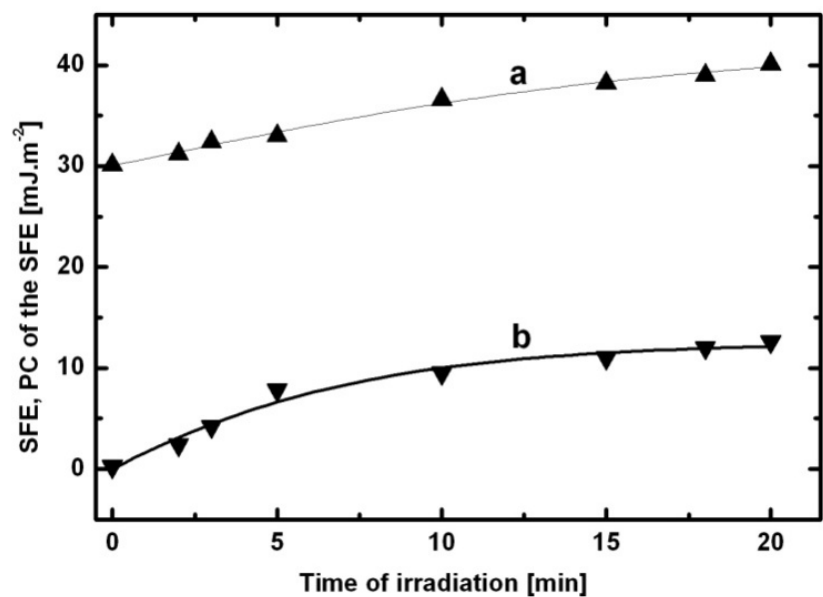


Fig. 27. Variation of the surface energy and its PC of iPP pre-treated by UV/POCl3 with the time of UV exposure ( $d_{UV} = 50$  mm): a - surface energy, b - PC of the surface energy

3.4 Modification by halogenization

Surface modification of iPP in vapours of halogen compounds (Novák & Chodák, 2001; Novák & Chodák, 2001; Kharitonov, 2000; Novák& Chodák, 2001; Hruska & Lepot, 2000; Carstens et al., 2000) 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 vapours of phosphoryl chloride on the iPP surface. UV-irradiation results in a faster decomposition of the halogen compound and leads to the UV-oxidation of the surface of polymer. Surface modification of iPP vapours of phosphoryl chloride under UV irradiation



(UV/ $\text{POCl}_3$ ) (Novák & Chodák, 2001; Novák & Chodák, 1999) 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 active chlorine, which takes part in the free radical reactions with PO macromolecules leading to a formation of  $-\text{POCl}_2$  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.

The surface and adhesive properties of iPP modified by UV radiation in the presence of  $\text{POCl}_3$  have been studied. Modification of iPP by UV/ $\text{POCl}_3$  results in an increase in surface energy of polymer as well as in an improvement of the mechanical work of adhesion of modified iPP to more polar polymers.

Fig. 27 illustrates a non-linear increase of the surface energy (curve a) and its PC (curve b) for iPP modified by UV/ $\text{POCl}_3$  in the dependence on the time of modification at the UV source distance of 50 mm. The surface energy for non-modified polymer was  $30.1 \text{ mJ.m}^{-2}$ . The surface energy and its PC of iPP pre-treated by UV/ $\text{POCl}_3$  increased non-linearly with time up to the value  $40.1 \text{ mJ.m}^{-2}$  after 20 minutes. The PC of the surface energy of modified iPP increased after 20 min. of modification from  $0.25 \text{ mJ.m}^{-2}$  up to  $12.6 \text{ mJ.m}^{-2}$ . The time-dependence of the PC of the surface energy (Fig. 27, curve b) leveled off after an initial increase enduring about 10 min. As expected, the strength of adhesive joints of modified iPP increases in accordance with the degree of hydrophilicity of modified polymer. Thus, adhesive properties of polymer are strongly related to the values of the PC of the surface energy.

The surface energy of iPP modified by UV/ $\text{POCl}_3$  was essentially higher in comparison with non-modified polymer. A non-linear increase of the surface energy and its PC against time of UV exposure was observed. The pre-treatment of iPP by UV/ $\text{POCl}_3$  method leads to a considerable growth in the surface and adhesive properties of the polymer 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/ $\text{POCl}_3$  modified iPP correspond with the measured values of the PC of the surface energy. The efficiency of iPP modification by UV/ $\text{POCl}_3$  substantially increased by diminishing the distance of UV radiation source from the surface of polymer or by increasing the intensity of UV source.

#### 4. Conclusion

The selection and application of modification procedure for the enhancement of adhesion properties of iPP depends mostly on the specific demands required on the adhesive joints in practice. When deciding about suitability of the modification method a detailed knowledge about physical and chemical changes undergoing on the surface, experimental demands and also aggressiveness of the reagents employed is needed. Based on this point of view the most practical surface treatments are the flame and electric discharge treatments which enables a continual modification during the processing, for instance in printing. This modification meets also the demand on a fast processing of the treated surface. On the other hand some very effective modification methods such as the modification by chromyl chloride vapours or phosphorus trichloride with UV light application are less popular because of implausibility of the modification reagents, in spite of the lasting effect of the modification. The surface modification of iPP is observed in a very narrow layer not

exceeding thickness of 10  $\mu\text{m}$  and is easily destroyed by heat or friction by which the effect of modification disappears. For practical purposes according to this reason, there is also suitable method of modification based on the modification of polymer in bulk consisting of the addition of polar low-molecular compound or a polymer respectively. As a matter of fact, the most efficient method of modification is grafting, e.g. by maleic anhydride, acrylic or itaconic acid, as well as the modification by block copolymers of the A-B-C type where A is a polar monomer and B is non-polar one. This modification is now intensively studied because it enables us to obtain good properties of iPP without significant deterioration of its physico-mechanical properties.

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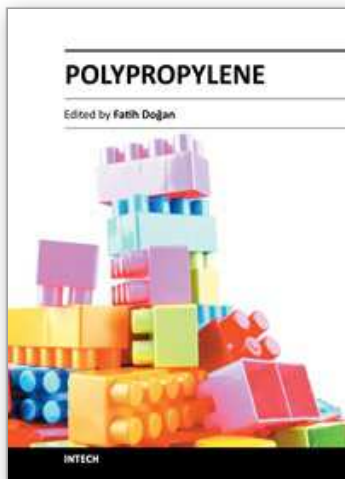
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## **Polypropylene**

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This book aims to bring together researchers and their papers on polypropylene, and to describe and illustrate the developmental stages polypropylene has gone through over the last 70 years. Besides, one can find papers not only on every application and practice of polypropylene but also on the latest polypropylene technologies. It is also intended in this compilation to present information on polypropylene in a medium readily accessible for any reader.

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