

Surface Energy and Adhesive Properties of Polyamide 12 Modified by Barrier and Radio-Frequency Discharge Plasma

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Summary. The polyamide 12 foil with sufficient surface and adhesive properties to other substrates can be prepared by discharge plasma modification. For improvement of bonding and printing of polymer a surface barrier discharge plasma in N₂ and O₂ as well as a radio-frequency discharge plasma in air has been studied. A significant increase in surface energy of the polymer as well as in strength of adhesive joint to more polar polymer was found. The chemical changes of PA 12 modified by plasma were analyzed using fourier transform infra red – attenuated total reflection (FTIR–ATR) spectroscopy, and X-ray photoelectron spectroscopy (XPS) measurements. The observed changes of surface properties of the polymer due to aging were not important.

Keywords. Adhesion; Surface; Polyamide; Plasma; Oxidation.

Introduction

Surface energy is an important property for applications of polymers. The low surface energy of polyamide 12 causes that its adhesive properties are insufficient for bonding and printing. The poor adhesion of PA 12 to more polar polymers and other substrates represents a problem, which can be solved with modification of the polymer. The printing on surface of the polymer requires that the wetting substances in liquid state have a lower surface energy value than the polymer. For this reason, the securing of good adhesion of printing inks or adhesives to PA 12 surface necessitates to raise its surface energy by a convenient method of modification. The most advanced method of modification of PA 12 surface, due to its practical usability, suitability to continuous modification processes, and efficiency of the modification, is based on modification by electric discharge plasma [1–6]. If this method of modification is applied the original suitable mechanical properties of the polymer remain preserved while the surface energy and polarity of the polymeric surface simultaneously increase [7–16].

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PA 12 foils were modified by surface barrier discharge (SBD) plasma at atmospheric pressure in O₂ or N₂ [7–9] and/or by radio-frequency discharge (RFD) plasma in air at reduced pressure of 26 Pa. The surface of PA 12 was modified by SBD plasma at various conditions.

The aim of the contribution is the study of the changes in surface and adhesive properties of PA 12 modified using SBD plasma in N₂ or O₂ at atmospheric pressure and RFD plasma in air at reduced pressure. The attention is devoted also to the changes in surface properties of modified PA 12 due to aging of the modified polymer.

Results and Discussion

The results of the study of surface and adhesive properties of PA 12 modified by SBD and RF discharge plasma are presented in Table 1 and in Figs. 1–4.

The surface properties of PA 12 foils modified by SBD plasma in O₂ and N₂ as well as by RFD plasma in air at reduced pressure *versus* time of modification are summarized in Table 1. The surface energy and its polar component of PA 12 modified by SBD plasma increased in the case of modification in N₂ (10 s, 60 s) in comparison with unmodified polymer. The changes of surface energy of PA 12 treated by SBD plasma were small. The surface energy of PA 12 modified by SBD plasma increased from 34.8 mJ · m⁻² (unmodified polymer) to 49.0 mJ · m⁻² (N₂ plasma, 10 s), and to 50.2 mJ · m⁻² (N₂ plasma, 60 s). The surface modification of PA 12 by discharge plasma with longer time of modification was more pronounced. The modification of polymer by SBD plasma in O₂ was less efficient in comparison to N₂ plasma. The surface energy of PA 12 pre-treated by RFD plasma at reduced pressure in air was higher considering polymer modified by SBD plasma. The surface energy of PA 12 treated by RFD plasma reached the value 54.6 mJ · m⁻² (air, 60 s).

The polar component of the surface energy of PA 12 after modification by SBD increased significantly from the value 7.1 (unmodified polymer) up to 25.4 mJ · m⁻² (SBD, N₂, 60 s) or 21.0 mJ · m⁻² (SBD, O₂, 10 s), and 33.7 mJ · m⁻² (RFD, air, 60 s), respectively. However, the dispersive component of the surface energy of PA 12 modified by SBD and RFD plasma, excepting the sample modified by RFD in air, 60 s, did not change significantly.

Table 1. Surface properties of PA 12 modified by SBD and RFD plasma for various gases and various times of activation

Activation time/sec	Atmosphere	Surface energy mJ · m ⁻²	Polar component mJ · m ⁻²	Dispersive component mJ · m ⁻²
0	–	34.8	7.1	27.7
10	SBD, O ₂	47.2	21.0	26.3
60	SBD, O ₂	46.1	15.9	30.2
10	SBD, N ₂	49.0	22.2	26.8
60	SBD, N ₂	50.2	25.4	24.8
10	RFD, Air	52.2	28.0	24.2
60	RFD, Air	54.6	33.7	20.9

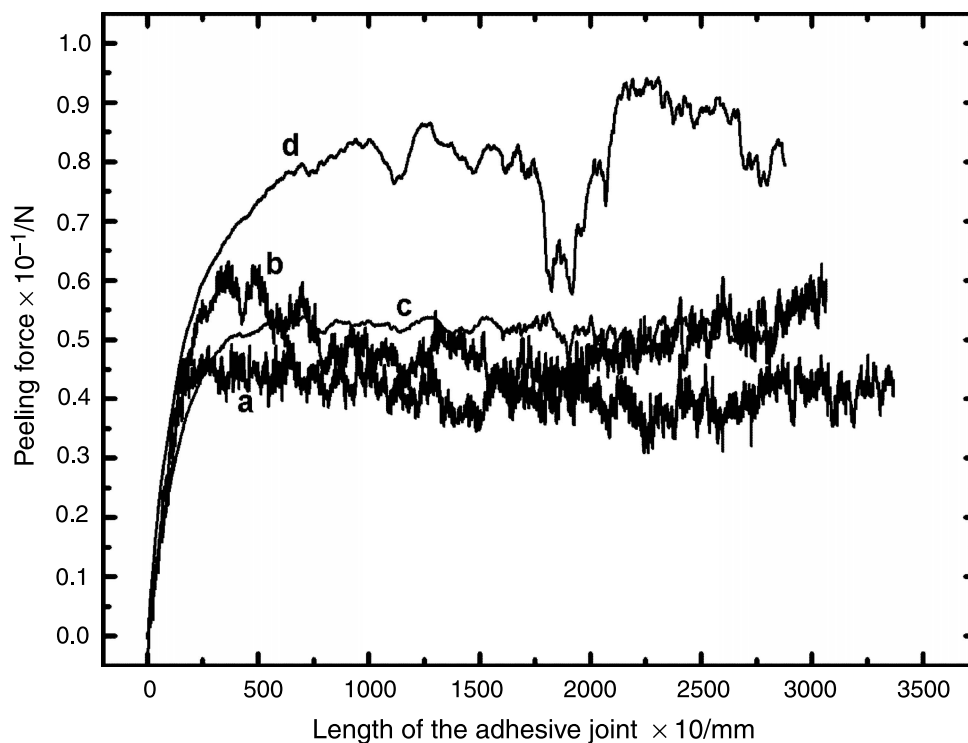


Fig. 1. Medium peeling force for *PA 12* modified by SBD and RFD plasma to polyacrylate vs. length of adhesive joint: a – unmodified polymer; b – SBD, 60 s, N_2 ; c – SBD, 60 s, O_2 ; d – RFD, 60 s

Figure 1 represents the dependence of peeling force of *PA 12* modified by SBD plasma at atmospheric pressure in O_2 and N_2 atmosphere and by RFD plasma at reduced pressure in air to polyacrylate on length of the adhesive joint.

According to Fig. 1 surface energy of *PA 12* increased significantly after modification by plasma, from 4 N up to 8–9 N. This growth of peeling force depends on kind of the used discharge plasma (SBD, RFD) as well as on the sort of the gases if SBD is applied. The changes in “peel spectra” in Fig. 1 reflect the non-homogeneities (or defects) present in adhesive joint. However, unmodified *PA 12* (plot a) also gives the peel spectra, which reflect occurrence of the defects on surface of the *PA 12* foils. RFD plasma in air (plot d) and SBD plasma in O_2 (plot c) provided the peel spectra (plot b and c) of modified *PA 12*, which were smoother comparing with spectra for unmodified polymer (plot a), and polymer modified by SBD plasma in N_2 (plot b).

Influence of peel strength of the adhesive joints of *PA 12* modified by SBD and RFD plasma to polyacrylate on time of activation is shown in Fig. 2. The peel strength of *PA 12* modified by plasma to polyacrylate increased more significantly with time of activation in the case of modification of polymer with RFD plasma than with SBD plasma.

The peel strength of adhesive joint increased from $0.12 N \cdot mm^{-1}$ (unmodified sample) to $0.14 N \cdot mm^{-1}$ (SBD, 60 s, N_2), $0.16 N \cdot mm^{-1}$ (SBD, 60 s, O_2), and $0.26 N \cdot mm^{-1}$ (RFD, 60 s). According to this figure, it is evident that values of peel strengths of adhesive joints were higher in the case of RFD, at shorter times of

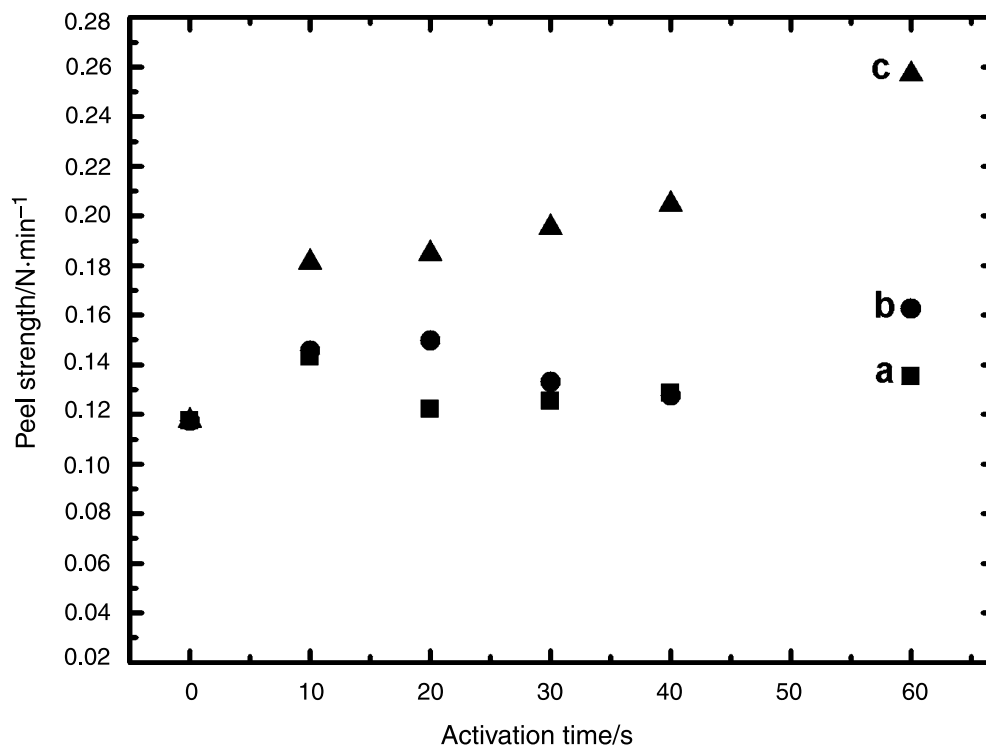


Fig. 2. Peel strength of PA 12 modified by discharge plasma to polyacrylate vs. time of activation for various atmospheres: a – SBD, 60 s, N₂; b – SBD, 60 s, O₂; c – RFD, 60 s

activation of PA 12 by plasma, in comparison with SBD plasma. The modification of PA 12 by SBD plasma was more efficient in O₂ atmosphere than in N₂ atmosphere. By Fig. 2 the further growth of the peel strength of adhesive joints in the system PA 12 – polyacrylate modified by RFD plasma with time of activation for times longer than 10 s was less intensive.

Figure 3 represents the FTIR–ATR spectra of PA 12 modified for various times of activation by RFD plasma at reduced pressure in air. The results of ATR spectra measurements reflect the changes in chemical structure of modified PA 12 due to activation by RFD plasma, and contain absorption bands of the functional groups generated during modification of the polymer by plasma in air. The absorption bands in Fig. 3 at 720–730 cm⁻¹ belong to CH₂ groups of the polymer, absorption bands at 1440 cm⁻¹ are caused by C–OH groups. In FTIR–ATR spectra of PA 12 modified by plasma the characteristic amide modes (amide-I band at 1637 cm⁻¹, amide-II band at 1555 cm⁻¹) have been observed. The FTIR–ATR spectra show the changes in chemical structure of PA 12 modified by RFD plasma in air, and contain the absorption bands of the oxygenic (*e.g.* carbonyl) functional groups with not very intensively developed peaks at 1715 cm⁻¹ (C=O groups) [15]. The identification of C=O bands in FTIR–ATR spectra was limited because the used KRS 5 (thallium-bromide-iodide) crystal didn't allow to use a higher pressure on PA 12 foil. A difference between the intensity of this absorption band between unmodified polymer and polymer treated by RFD plasma was found. The activation of PA 12 (plot a) foil

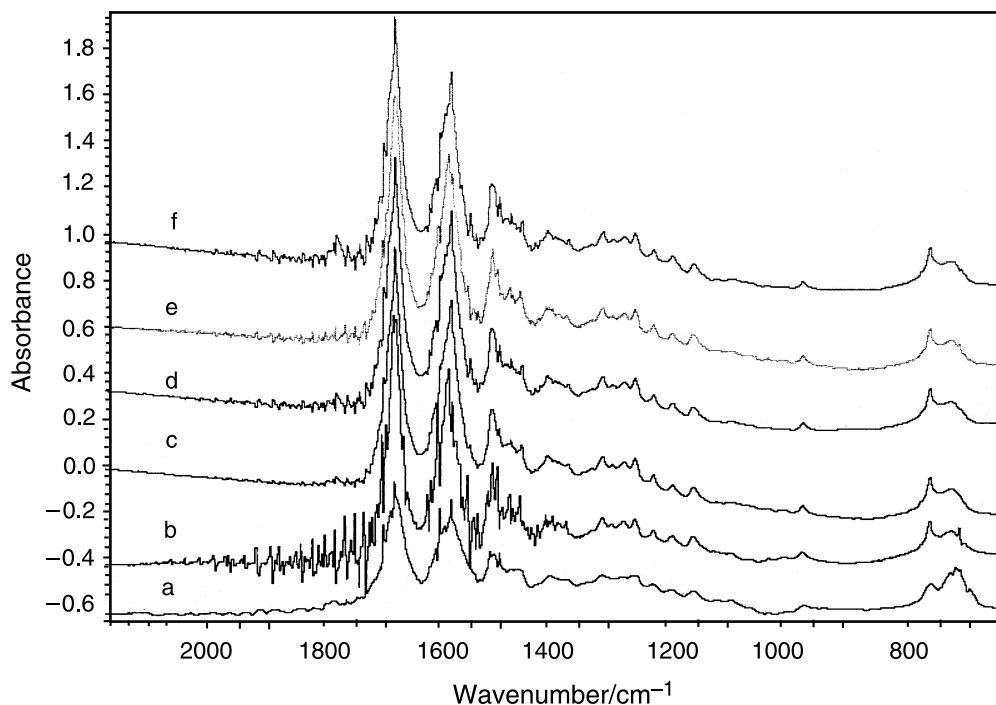


Fig. 3. FTIR-ATR spectra of PA 12 modified by RFD plasma in air at reduced pressure for various time of modification: a – untreated sample, b – 10 s; c – 20 s; d – 30 s; e – 40 s; f – 60 s

by RFD plasma results in creation of oxidizing, *i.e.* carbonyl functional groups (plots b, c, d, e, f) with absorption bands at 1715 cm^{-1} . The interpretation of the results from FTIR-ATR spectra in the investigated region is more complicated due to presence of water humidity. The presence of oxygenic groups in the PA 12 modified by plasma was confirmed by another independent method, XPS measurement, whereas the O/C atomic ratio increased due to modification of polymer by plasma from the value 0.163 (unmodified polymer) to 0.219 (PA 12 modified by plasma) (Fig. 5 and Table 2).

The reduction of surface energy and its polar component of PA 12 modified by SBD plasma (10 s, 50 W, N_2) is shown in Fig. 4. The value of the surface energy (Fig. 4, plot a) of PA 12 modified by SBD plasma in the course of aging did not change significantly. The surface energy after 30 days of aging decreased only by 5% compared with freshly pre-treated PA 12, *i.e.* from $49\text{ mJ}\cdot\text{m}^{-2}$ (for freshly modified polymer), up to $46.5\text{ mJ}\cdot\text{m}^{-2}$ (for 30 days aged polymer). The changes of the surface energy of PA 12 modified by SBD plasma occurred mainly due to the decrease of polar component of the surface energy (Fig. 4, plot b).

The polar component of the surface energy after 30 days of aging diminished from $22.2\text{ mJ}\cdot\text{m}^{-2}$ (neat polymer) to $19.5\text{ mJ}\cdot\text{m}^{-2}$ (after 30 days of aging). The surface rearrangement process of the polymers (*e.g.* polyolefins) modified by discharge plasma is well known. The polar oxygen-containing surface groups in modified polymer are buried in the bulk by the polymer segment mobility in order to minimize the surface energy with surrounding phase. At the same time, the diffusion

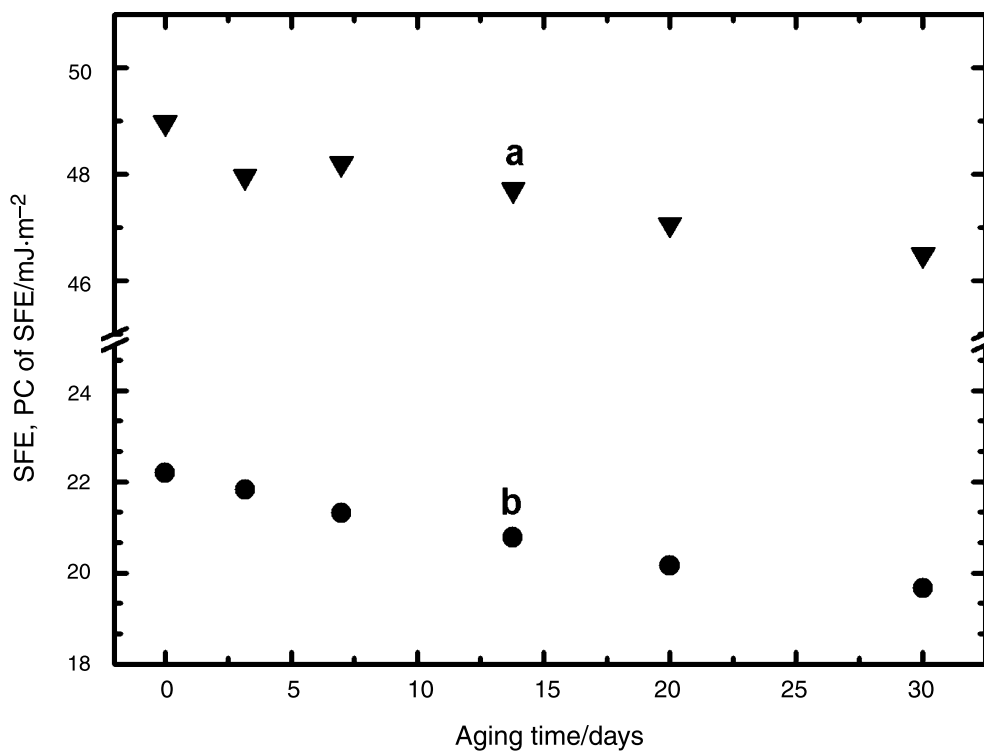


Fig. 4. Surface energy and its polar component of PA 12 modified by SBD plasma in N₂ (10 s, 50 W) vs. time of aging

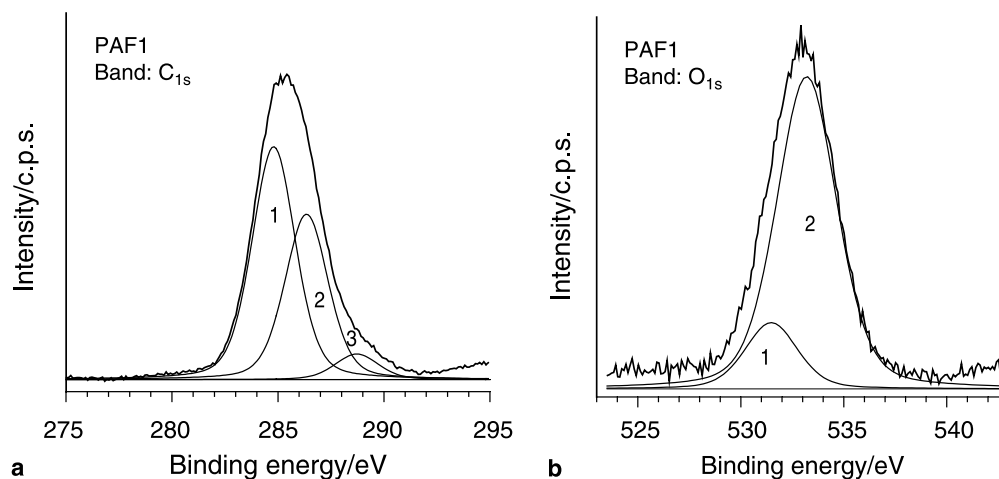


Fig. 5. XPS measurements – the narrow regions of untreated PA 12: a – C_{1s}, b – O_{1s}

of the unmodified polymeric chains, oligomers, as well as manufacturing additives to the surface of the polymer is going on. The physical changes (functional groups reorientation, diffusion) reduce the polarity of the PA 12 surface modified by plasma in the course of aging. The chemical changes on the polymeric surface take an

Table 2. Results of XPS measurements of PA 12 modified by SBD plasma in O₂

Sample	Untreated PA 12			Treated PA 12 (SBD, O ₂ , 60 s)		
	BE	(FWHM)	N	BE	(FWHM)	N
C _{1s}	284.8	(2.4)	73672	284.8	(2.9)	60680
	286.4	(2.4)	52503	286.4	(2.6)	60783
	288.8	(2.4)	8101	288.8	(2.6)	10559
			134276			132022
N _{1s}	399.4	(3.0)	963	399.3	(2.9)	2958
	400.9	(3.0)	5904	401.0	(2.9)	8174
			6867			11132
			14034			11132
						26.6%
						73.4%
O _{1s}	531.5	(2.9)	3405	531.5	(3.0)	7786
	533.2	(2.4)	18433	533.3	(3.3)	21073
			21838			28859
N/C			0.051			0.084
O/C			0.163			0.219
O + N/C			0.214			0.303
N/O			0.314			0.386

important role due to chemical reactions changing the unstable oxygenic functional groups to more stable products (changes of unstable peroxidic and hydroperoxidic groups to more stable ketonic and carboxylic groups). The hydrophobic recovery of PA 12 modified by plasma from the initial modification is far lower and more slowly in comparison with other polyamides, *e.g.* PA 6 [16]. Due to the incompatibility of the polar low-molecular oxidized material created during modification of PA 12 by plasma and the non-polar hydrocarbon at the polymer surface, the diffusion of these species into the PA 12 bulk is probably impossible. The semi-crystalline nature of PA 12 provides additional cohesive energy *via* intermolecular hydrogen bonding strengthening the crystalline regions of the polymer. The effect of the barrier discharge plasma is more pronounced in amorphous regions of PA 12 with structural irregularities and creation of polymer regions with less structural irregularities results in more durable and stable surface modification of the polymer.

The results of XPS study of untreated PA 12 are shown in Fig. 5. It presents the dependence of intensity *versus* binding energy for C_{1s} (a) and O_{1s} (b) narrow regions of untreated PA 12. The reconstructed C_{1s} spectrum for untreated PA 12 consists of three peaks. The spectrum at the binding energy of 284.8 eV is attributed to the aliphatic carbon atoms (C¹; C–H). The peak at 286.4 eV is assigned to the carbon atoms bonded to the –NH– groups (C²; C–N), and the peak at 288.8 eV corresponds to the carbon atoms of carbonyl groups (C³; C=O). The O_{1s} spectrum having two components (Fig. 5b) was reconstructed by peak fitting gives the chemical composition of untreated PA 12. The peak at 531.5 eV (O¹) corresponds to the carbonyl oxygen present on the surface of untreated sample. The peak at 533.2 eV (O²) corresponds to oxygen atoms singly bonded to carbon atoms. The N_{1s} spectra consist also of two peaks at 531.5 eV and of 533.2 eV. While the untreated polymer

contains lower content of nitrogen-, or/and oxygen-groups, the C_{1s} regions of the plasma-treated PA 12 foils show new peaks of this kind in areas from 286 to 290 eV, and the data are summarized in Table 2, which contains the binding energy (BE), the full width at half-maximum (FWHM) of the peaks, and the relative content of the atomic species (N) on the surface of PA 12 determined by considering the integrated peak areas of C_{1s} and O_{1s} bands and their sensitivity factors, respectively. The O/C atomic ratio increased due to modification of PA 12 by plasma from the value 0.163 (unmodified polymer) to 0.219 (modified PA 12), *i.e.* the amount of oxygen in PA 12 due to modification by plasma increased by 30% as compared to unmodified polymer. This change affects the C_{1s} and O_{1s} fine structure (Fig. 5a, peak C^3 ; Fig. 5b, peaks O^1 and O^2). However, amounts of O and N in PA 12 modified by plasma given in Table 2 increased also significantly, *e.g.* the N/C ratio after modification of PA 12 by SBD plasma increased from 0.051 to 0.084, O + N/C ratio from 0.214 to 0.303, and N/O increased from 0.314 to 0.386.

Conclusions

A significant increase in surface energy and its polar component of PA 12 modified by SBD plasma in O_2 and N_2 at atmospheric pressure and RFD plasma in air at reduced pressure was confirmed. This increase in surface properties of the polymer was important for short time (10 s) of modification by plasma, and for longer time of modification was more pronounced. The differences between surface energy and its polar components of modified PA 12 for various methods of modification by plasma were not significant. The medium peeling force of PA 12 modified by plasma increased in comparison with unmodified polymer in dependency on the kind of plasma. The decrease of the peel strength of adhesive joint of modified PA 12 to polyacrylate was observed by sequence: $P_{RFD,Air} > P_{SBD,O_2} > P_{SBD,N_2}$. The higher strengths of adhesive joints of modified PA 12 were observed in the case of modification of the polymer by RFD plasma, and lower in the case of SBD plasma modification. The FTIR-ATR spectra detected the changes in chemical structure of PA 12 modified by plasma and contained the development of the absorption bands of the oxygenic functional groups at 1715 cm^{-1} (C=O groups). The changes of the surface energy of PA 12 modified by SBD plasma in N_2 , occurring mainly due to reduction of its polar component during 30 days of aging, were very low probably due to strengthening the crystalline regions of the polymer *via* intermolecular hydrogen bonding. It was shown that modification of PA 12 by barrier discharge plasma led to the more durable and stable pre-treatment of this polymer. The XPS reflects a significant increase of oxygen containing groups on the surface of the modified polymer. The increase in strength of adhesive joints of PA 12 modified by plasma to more polar polymer correlates with XPS results due to enhancement of hydrophilic functional groups on the polymeric surface.

Experimental

Used Polymers

The experiments were carried out with polyamide 12 (PA 12, Rilsan 12, Atofina, France) with a thickness of 0.05 mm, density (23°C) = $1.01\text{ g}\cdot\text{cm}^{-3}$, and melting temperature = $174\text{--}178^\circ\text{C}$. The

adhesive joints modified PA 12 – polyacrylate were prepared by using poly(ethyl hexyl acrylate) (Polysciences, USA) solution in ethyl acetate (Fluka, SRN) deposited on biaxially oriented isotactic polypropylene (Slovnaft, Chemosvit, Slovakia) support foils with a thickness of 0.02 mm.

Modification of Polymer

The modification of PA 12 foils by SBD plasma was performed in a laboratory reactor at atmospheric pressure in N₂ or O₂ of a technical purity. The SBD generator consists of alumina-based insulating layer from one side fully covered with metal electrode. On the other side of the insulating plate was an 80 × 80 mm metal electrode consisting of strips 80 mm long and 1 mm wide. The barrier discharge appears along the insulator surface in a decreasing initial electric field. The samples in the glass vessel were modified at atmospheric pressure in various gases. The voltage of SBD reactor was 100 V, current density 1 A, and frequency was 6 kHz.

The radio-frequency discharge (RFD) was used at reduced pressure 26 Pa in various gases, and produced the high homogeneity plasma. The device consists of stainless steel locked-up vacuum vessel with two circular parallel plate electrodes having a diameter of 240 mm, and the distance between electrodes was 40 mm. The voltage of RFD source was 1000 or 2000 V, current density 0.1 A, and frequency was 13.56 MHz.

Methods of Measurements

Strength of Adhesive Joints

The strength of adhesive joints in the modified PA 12 – polyacrylates was measured by peeling of the joints under the angle of 90° on universal testing machine Instron 4301 (Instron, England). The measurement was carried out using an aluminum-peeling wheel in which the adhesive joints were fixed. The peeling of adhesive joint proceeded at speed of 10 mm · min⁻¹, the length of joint was 100 mm. The strength of adhesive joint, P (N · mm⁻¹), was calculated from Eq. (1) where F_s is mean force of peeling (N), d is width of adhesive joint (mm).

$$P = \frac{F_s}{d} \quad (1)$$

The deposition of polyacrylate solution in ethyl acetate was performed using a coating ruler (Dioptra, Czech Republic) with a thickness of the layer of 0.12 mm.

Surface Properties

Measurement of the surface energy of polymer was carried out by direct measurements of contact angles of testing liquids set (re-distilled water, ethylene glycol, formamide, methylene iodide, 1-bromonaphthalene) on microscopic Contact Angle Meter (Zeiss, Germany). The dependence of contact angle *versus* time was extrapolated to $t=0$ and the surface energy and its polar component were evaluated by *Kinloch* equation (Eq. (2)) based on method of least squares [3] where θ = contact angle (deg), γ_{LV} = surface energy of the testing liquid (mJ · m⁻²), $\gamma_{LV}^d, \gamma_{LV}^p$ = dispersive and polar components of surface energy of the testing liquid (mJ · m⁻²), and γ_s^d, γ_s^p = dispersive and polar component of surface energy of the polymer (mJ · m⁻²).

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

FTIR–ATR Spectroscopy

FTIR–ATR measurements of the samples (PA 12 films) were performed on NICOLET Impact 400 FTIR spectrometer (Nicolet, USA). A resolution of 4 cm⁻¹, a scan range of 4000–400 cm⁻¹, and a total of 512 scans per analysis were used. The KRS 5 crystal (thallium-bromide-iodide) has been used for FTIR–ATR measurements.

XPS Measurements

The chemical surface changes on the surface of synthetic polymer systems after plasma treatment were studied by XPS measurements using a VG ESCA 3 instrument (Poland Academy of Sciences, Poland).

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