

## Modification of the polyamide foil by Diffuse Coplanar Barrier Discharge plasma for furniture applications

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**Abstract:** *Modification of the polyamide foil by Diffuse Coplanar Barrier Discharge plasma for furniture applications.* The surface free energy of polyamide foil is insufficient in some applications, e.g. bonding of foils for furniture applications with polyurethane dispersions at vacuum pressing. The plasma treatment significantly improves surface properties. Experiments proved an increase of the surface free energy, peel strength and change of chemical composition of the foil surface.

*Keywords:* polyamide foil, furniture surface finishing, plasma treatment

### INTRODUCTION

The low surface free energy of polyamides can be greatly increased by using various methods of the surface modification (1-5) by the atmospheric discharge plasma. The application of polyamides in the automotive, human medicine as well as in furniture production (e.g. foil surface finishing) needs to increase the surface free energy of the polymer using the suitable modification method, e.g. by Diffuse Coplanar Surface Barrier discharge (DCSBD) plasma. Pre-treatment by DCSBD plasma presents a dry process used frequently for industrial purposes, e.g. for an increase of adhesion of polyamide veneer to wood in the furniture industry. Polyamide (PA) 6 is the most widely used a semi-crystalline engineering thermoplastic polymer having a good thermal stability, and mechanical properties. PA 6 macromolecules show amphoteric character due to two kinds of polar functional groups, i.e. amino and carboxylic groups. PA 6 is classified as hydrophobic polymer in many applications. Modification of PA 6 by cold plasma (5,6) is usually confined to several 10 nm, and does not influence bulk properties of the polymer.

Reactions between species of processing gases and surface species of PA 6 produce new functional groups on the surface. The oxygen-containing plasma modification of the polymer leads to the creation of various oxygenic functional groups significantly increasing the hydrophilicity of PA 6.

### EXPERIMENTAL

#### *Used polymers*

PA 6 foils – nature ZellamidTM (Zell-Metall, Kaprun, Austria), density = 1.14 g.cm<sup>-3</sup>, area mass = 0.65 kg.m<sup>-2</sup>, foil thickness  $d = 0.5 \pm 0.03$  mm,  $T_m = 226$  °C. The PA 6 foils were dried during 24 hours at  $T = 110$  °C, and subsequently were conditioned in the glass vessel at RT, and relative humidity of 40 %.

#### *Method of surface modification by plasma*

The modification of PA 6 foils by Diffuse Coplanar Surface Barrier discharge (DCSBD) plasma was performed in a laboratory of the plasma source at atmospheric pressure in medium of N<sub>2</sub> and O<sub>2</sub> gas of the technical purity. The voltage of DCSBD plasma generator was 6 kV, current density = 1 A, and frequency = 6 kHz.

### *Measurement methods*

#### *Surface free energy*

The surface free energy of PET was determined via measurements of contact angles of a set of testing liquids (i.e. re-distilled water, ethylene glycol, formamide, methylene iodide, 1-bromonaphthalene) using SEE (Surface Energy Evaluation) system completed with a web camera (Masaryk University, Czech Republic) and necessary PC software. The drop of the testing liquid ( $V = 3 \mu\text{l}$ ) were placed with a micropipette (0 - 5  $\mu\text{l}$ , Biohit, Finland) on the polymeric surface, and a contact angle of the testing liquid was measured.

The surface free energies of the polymer were evaluated by the Owens-Wendt-Rabel-Kaelble (OWRK) equation modified by the least squares method (3).

#### *Peel strength of adhesive joint*

The peel strength of the adhesive joint (P) to poly acrylate was found by 90° peeling of the adhesive joint using a universal testing machine Instron 4301 (Instron, England) with 100 N measuring cell. The adhesive joints were fixed in an aluminium peeling circle. The width of the adhesive joint was 20 mm, and length was 160 mm. The adhesive joints were prepared from modified PA6 foils and biaxially oriented isotactic polypropylene foils impregnated with solution of polyacrylate. The peeling speed of the adhesive joint was 1.5 mm.min<sup>-1</sup>.

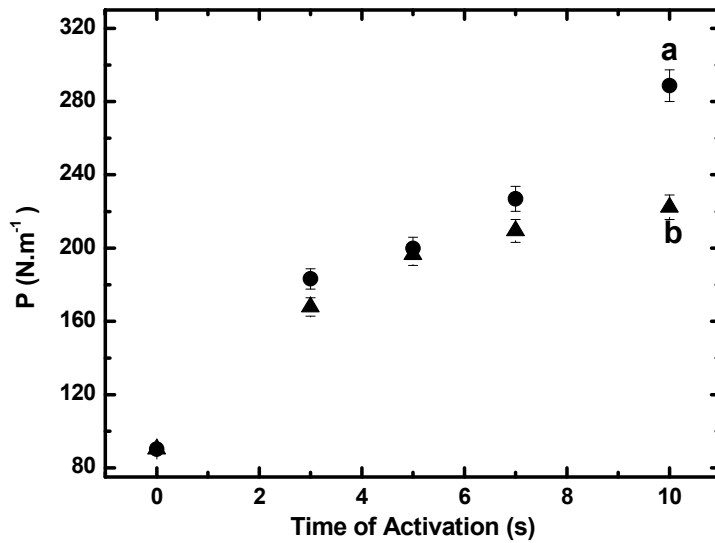
#### *X-ray photoelectron spectroscopy (XPS)*

XPS analysis was performed by Kratos XSAM 800 equipment, with Mg K $\alpha_{1,2}$  radiation, in fixed analyser transmission mode, with 80 and 40 eV pass energies for the wide scan and the detailed spectra, respectively. Data acquisition and processing were done with the Kratos Vision 2 program. Spectra were referenced to the hydrocarbon type C1s component set at a binding energy of 285.0 eV.

## RESULTS AND DISCUSSION

#### *Peel strength of adhesive joint*

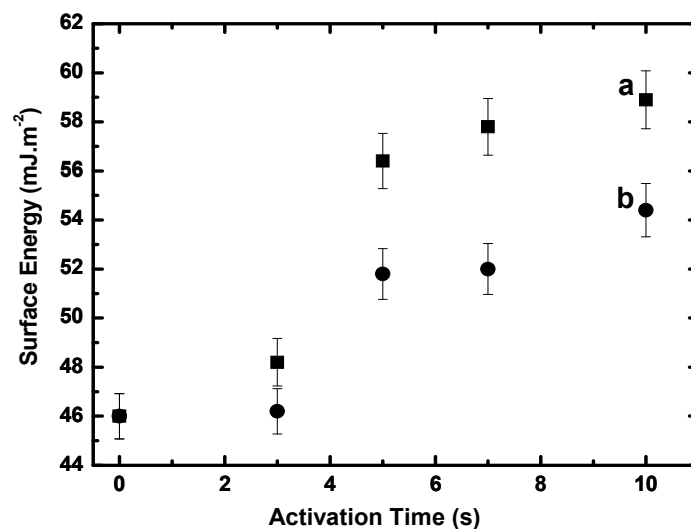
The results of the peel strengths of adhesive joints modified PA6 foils – polyacrylate are summarized in Figure 1. Figure 1 shows the peel strength of adhesive joint modified by DCSBD plasma in O<sub>2</sub> and N<sub>2</sub> to poly acrylate in dependence on time of activation by plasma is shown. According to Figure 1, the peel strength of the adhesive joint intensively increased up to 10s of the PA 6 activation by plasma from the value of 90 N/m (neat polymer) up to 222 N/m (N<sub>2</sub> plasma) or 289 N/m (O<sub>2</sub> plasma). The differences between peel strengths of adhesive joints for both used gases are negligible up to 7s of the PA 6 modification by DCSBD plasma. For longer modification times, i.e. 10s, the value of the peel strength seems to be significantly higher if O<sub>2</sub> plasma was used in comparison with N<sub>2</sub> plasma. This finding should be explained with more intense surface oxidation of PA 6, and polarity of the surface, if O<sub>2</sub> as a processing gas was used.



**Fig. 1** Peel strength of the adhesive joint of PA 6 modified by DCSBD to polyacrylate plasma vs. time of activation by plasma: a – oxygen, b – nitrogen

### Surface free energy

The dependencies of the surface free energy of PA 6 modified by DCSBD plasma determined by the contact angle measurements using the OWRK (Owens-Wendt-Rabel-Kaelble) method are shown in Figure 2. The surface free energy of PA 6 modified by DCSBD plasma increases significantly from 46.0 mJ.m<sup>-2</sup> (unmodified polymer) up to 58.9 mJ.m<sup>-2</sup> (DCSBD plasma, 10 s, O<sub>2</sub>), and 54.4 mJ.m<sup>-2</sup> (DCSBD, 10 s, N<sub>2</sub>). The pre-treatment of PA 6 by DCSBD in oxygen plasma was by Figure 2 more efficient than in N<sub>2</sub> plasma.



**Fig. 2** Surface free energy (by OWRK) of PA 6 modified by DCSBD plasma vs. time of activation: a – oxygen, b – nitrogen

### XPS measurements

The changes of the surface composition upon DCSBD plasma treatment time (Figure 3) show a steady increase of O- and N-contents, and a corresponding decrease of the C-

content. Simultaneously, the surface O/C and N/C ratios increase, while the O/N ratio decreases strongly with the treatment time. After 10 s of N<sub>2</sub> plasma treatment, the N-content changes from 2.5 to 10.4 at.% and that of O-content from 10.2 to 16.5 at.%. The above results suggest the elimination of the surface contamination layer. In addition, a definite incorporation of oxygen can be deduced, because the surface O-content determined after 10s of treatment (16.5 at.%) exceeds significantly the O-content pertaining to clean untreated PA 6 (12.5 at.%). The observed increase of O-content can be either due to a direct O-incorporation or due to the hydrolysis of the C=N bonds created upon a previous N-incorporation. Such a hydrolytic reaction is known to be fast and is known to lead to the creation of carbonyl groups.

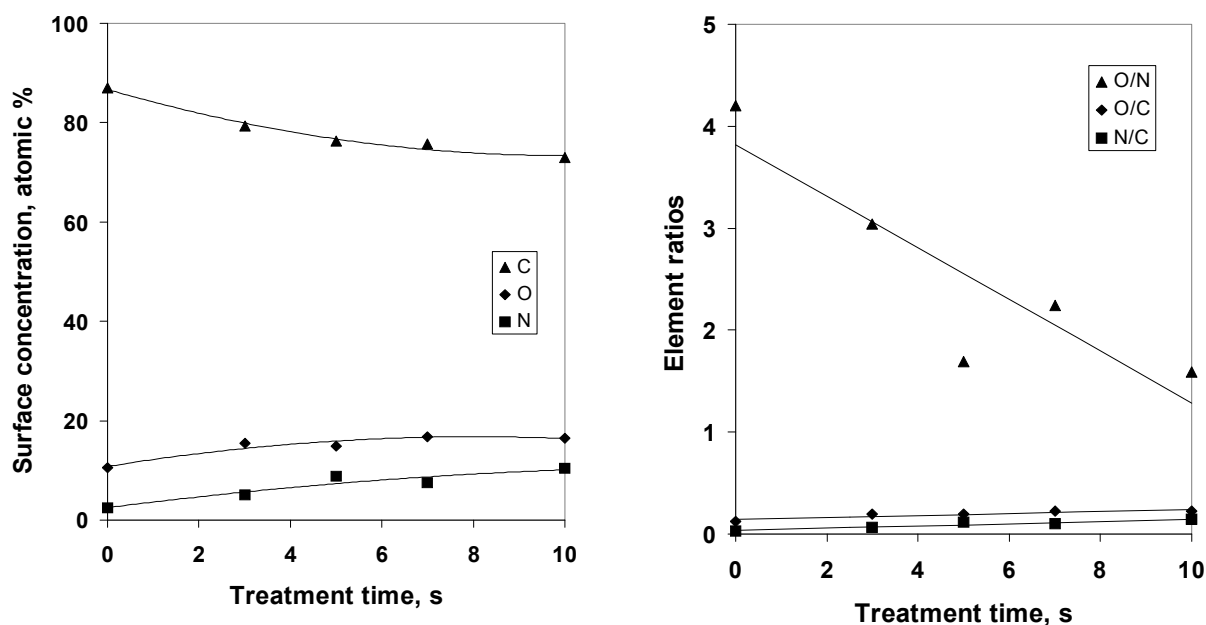


Figure 3. Surface composition (left) and element ratios (right) by XPS results vs. DCSBD plasma treatment time

## CONCLUSIONS

1. The peel strength of adhesive joint of PA 6 modified by DCSBD plasma increased significantly from the value of 90 N/m (neat polymer) up to 220 N/m (N<sub>2</sub>, 10s) or 290 N/m (O<sub>2</sub>, 10s),
2. The surface free energy of PA 6 modified by DCSBD plasma increased significantly with the activation time from 46.0 mJ.m<sup>-2</sup> (neat polymer) up to 58.9 mJ.m<sup>-2</sup> (DCSBD, 10s, O<sub>2</sub>), and 54.4 mJ.m<sup>-2</sup> (DCSBD, 10s, N<sub>2</sub>). The pre-treatment of PA 6 by DCSBD oxygen plasma was more efficient regarding N<sub>2</sub> plasma,
3. XPS analysis of the nitrogen plasma-treated PA 6 shows a gradual increase of O-, and N-contents, and the corresponding decrease of the C-content. Within 10s of the plasma-treatment, the N-content increases from 2.5 to 10.4 at.%, and that of O from 10.2 to 16.5 at.%,

## REFERENCES

1. POLETTI G., ORSINI F., RAFFAELE-ADDAMO A., RICCARDI C., SELLI E. 2003: Appl. Surf. Sci. 219, 311.
2. NOESKE M., DEGENHARDT J., STRUDTHOFF S., LOMMATZSCH U. 2004: Intern. J. Adhes. Adhesives 24, 171.

3. YANG P., DENG J.Y., YANG W.T. 2003: Polymer 44, 7157.
4. RÁHEL J., ČERNÁK M., HUDEC I., ŠTEFEČKA M., KANDO M., CHODÁK I. 2000: Plasmas Polymers. 5, 119.
5. ŠIMOR M., RÁHEL J., ČERNÁK M., IMAHORI Y., ŠTEFEČKA M., KANDO M. 2003: Surf. Coat. Technol.172, 1.
6. NOVÁK I., ŠTEVIAR M., CHODÁK I., KRUPA I., NEDELČEV T., ŠPÍRKOVÁ M., CHEHIMI M.M., MOSNÁČEK J., KLEINOVÁ A. 2007: Polymers for Advanced Technologies 18, 97.

**Streszczenie:** *Modyfikacja folii poliamidowej za pomocą wyladowania barierowego do zastosowań w meblarstwie.* Energia powierzchniowa folii poliamidowej jest niewystarczająca w niektórych zastosowaniach, takich jak opłaszczowanie przy pomocy dyspersyjnych klejów poliuretanowych. Aktywacja plazmowa znacząco poprawia własności powierzchni. Badania wykazały wzrost energii powierzchniowej, wytrzymałości na odrywanie oraz zmiany składu chemicznego folii.

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