Atmospheric pressure plasma treatment of polyamide-12 foils

Abstract: The surface of a polyamide-12 (PA-12) foil was modified in order to improve the adhesive properties by two types of atmospheric pressure plasma sources. The samples were characterized using contact angle measurement, adhesive properties measurement and X-ray photoelectron spectroscopy (XPS). The ageing of the plasma modification was also studied. A significant increase in wettability was observed at different treatment times. The same effect was also seen in the adhesive properties - the adhesion was increased almost 12 times for 10 s DCSBD treatment in comparison to untreated PA-12. XPS analysis confirmed chemical changes due to the plasma modification of the PA-12. It was concluded that both plasma sources improve the adhesive properties of PA-12, with DCSBD obtaining better results.

Keywords: PA-12, plasma treatment, contact angle, XPS, peel test

1 Introduction

Polyamides are increasingly used for many applications due to their unique properties such as abrasion resistance, resistance against greases, oils, fuels, water, etc. or high processability and flexibility. One of the most commonly used polyamide is polyamide-12 (PA-12), which can be found in many industrial applications such as protective coverings, flexible piping, ski boots, sealing rings or tubing and profiles for automotive industry. Although PA-12 is a thermoplastic material that is besides other things hard wearing and resistant to oils, water or greases. For some applications these traits are desirable, but for other industrial utilizations some of these properties can be a disadvantage and need to be suppressed. Poor hydrophilic properties affect paintability, printability, adhesion etc. and for this reason, a surface pre-treatment is required in order to gain sufficient adhesion.

The methods used to modify a polymer surface are highly various, they can be thermal, mechanical, chemical, photochemical [1-4] or plasma [5-7]. One of the most promising methods are plasma surface modifications, which are preferred procedures as they are considered environmentally friendly. Moreover, the plasma treatment enables surface modifications without changing the bulk properties of the treated material [8]. Plasma techniques are very flexible and may work under various conditions in order to cause intended effect.

Many investigations have been carried out using a low pressure or atmospheric pressure plasma to modify the surfaces. The first way is expensive due to the required vacuum apparatus and for the impracticality for industrial in-line processing. Atmospheric pressure plasma treatment may have many advantages; low costs (it could be installed directly into production line or experimental arrangements), and it is not limited in size for industrial purposes [9,10]. Therefore the recent studies concerning surface modification of polymers have been focused on atmospheric pressure plasma treatment [8-12].

In this paper two types of plasma sources, Diffuse Coplanar Surface Barrier Discharge (DCSBD) operated at atmospheric pressure in an ambient air and industrial corona were used to modify surface properties of PA-12. The modification of polyamide surface was investigated by means of contact angle measurement and X-ray photoelectron spectroscopy (XPS). The adhesive properties were analyzed using the peel test. Ageing
of the plasma modification of the modified polyamide surface was studied as well. The motivation for this study was to increase wettability of the polyamide foil in order to improve adhesion of the prints to the foil used as the upper part of a ski made by Sporten company (Czech Republic).

2 Experimental Procedure

Experiments were done on polyamide-12 foils from Sporten. Two types of atmospheric pressure plasma sources were used for plasma modification of the polyamide surface. Atmospheric pressure DCSBD was used as a source of non-equilibrium, macroscopically homogeneous plasma. The DCSBD electrode system consists of many parallel silver electrodes embedded in Al₂O₃ ceramics (Fig. 1) [13,14]. Plasma surface treatment of PA-12 foil was realized on one side in a static regime (the sample was slightly being pushed two or three times in order to secure homogeneity of plasma treatment) with an input power of 400 W (2.56 W cm⁻²), ambient air was used as a working gas at room temperature, and with different treatment times 5, 10, and 15 seconds. The DCSBD plasma source generates a very thin layer of plasma (~0.3 mm) with a very high plasma power density (~100 W cm⁻³) [15]. The distance between the sample and ceramics was kept 0.3 mm to secure good contact between plasma and the sample.

Plasma treatments were also carried out using a commercial device AHLBRANDT Industrial Corona System, which uses a volume configuration of electrodes isolated by a ceramic layer. Plasma burns between a rotating cylinder and a detachable electrode with gaps, which serve as an air outlet. Plasma was generated in an ambient air at atmospheric pressure, at room temperature and at the same square power density (2.56 W cm⁻²) as in the case of DCSBD. The samples were treated 5, 10 and 15 seconds. The polyamide foil was attached to the cylinder, whose average speed of rotation was 18 m min⁻¹. The distance between the sample and electrodes was 1 mm.

The analysis methods used for verification of the surface modification by DCSBD and industrial corona were: contact angle measurements, XPS measurements and adhesion measurements.

The contact angle was measured directly using the image of the sessile drops (2 µl) taken with the help of Surface Energy Evaluation System [16]. Distilled water was used as the testing liquid. To minimize a measurement error 12 contact angles were measured, with the highest and the lowest value eliminated. The final contact angle value was determined as an arithmetic average of the remaining 10 contact angle values.

The XPS measurements were performed with an ESCALAB 250Xi (ThermoFisher Scientific) using the AlKα X-Ray source operating at 200 W beam power (650 microns spot size). The survey spectra and high-resolution spectra were acquired using a pass energy of 50 eV and 20 eV, respectively. The resolution was set to 1 eV and 0.1 eV, respectively. In order to prevent surface charging electron flood gun was used. The Cls electron binding energy was referenced at 284.8 eV. The spectra calibration, processing and fitting routines were done using Avantage software.

The strength of adhesion was measured by peeling the adhesive tape away from the polyamide. The peel test was performed using a testing machine (Instron 4301) at a crosshead speed 10 mm min⁻¹ and with the length of the adhesive joint of 100 mm. A special clamp was used which allows for a 90° angle at joint during the entire test.

Figure 1: The photo of DCSBD electrode system on the left, the photo of industrial corona on the right.
3 Results and Discussion

The results of the surface and adhesive properties study of plasma modified PA-12 are summarized in Tables 1-2 and in Figs. 2-5.

3.1 Contact angle measurement

Fig. 2a presents the influence of the plasma treatment time on the wettability of the plasma modified PA-12. The significant decrease of water contact angle (63.34° for reference PA-12 foil) was observed after 5 s of the plasma treatment compared to untreated PA-12. Both samples modified by the DCSBD and by the industrial corona showed almost the same contact angle value (32.30° for DCSBD, 32.22° for industrial corona, respectively), although the samples treated by the DCSBD seem to be modified in a more homogeneous way. After 10 s of a plasma treatment there was no significant change of water contact angle using industrial corona modification. On the contrary the water contact angle of DCSBD modified PA-12 increased to 38.61°. For the longest plasma treatment time (15 s) the water contact angle of the industrial corona modified samples decreased to the lowest value of 26.54°, the water contact angle of the DCSBD treated PA-12 dropped to 34.49°.

Plasma surface modification is not entirely permanent and thus measuring of ageing of the plasma modification plays an important role. Fig. 2b shows how water contact angle changed with time after the plasma treatment (DCSBD and industrial plasma treatment) with 5, 10 and 15 seconds treatment times. As can be seen, the water contact angle considerably increased during the first day of ageing to the values in the range from 40° to 47° (with the exception of 5 s industrial corona treated samples, whose value remained almost the same). After 120 hours (5 days) the water contact angle, especially for DCSBD treated samples, reported very small changes. It was observed, that DCSBD modification of the PA-12 faded away slower than industrial corona modification. From the long-term point of view the ageing of surface modification of PA-12 is slower for the DCSBD treated samples. In this case the increased wettability was observed even after 1368 hours (2 months) of ageing (55.97°) for all treatment times, as shown in Fig. 3. The slower ageing of the surface modification using DCSBD plasma source can be explained by a more homogeneous modification than in the case of the filamentary industrial corona [17,18].

3.2 Adhesive properties

The peel strength closely relates to the surface free energy, roughness and chemical nature of studied material [8]. Therefore an increase of wettability should result in a peel strength increase. On the other hand, rougher surfaces result in a higher adhesion, thus adhesion need to be studied as a complex quantity. The information about adhesion changes were obtained from the peel test measurements that are shown in Fig. 4.

The strong increase in the peel strength of PA-12 foils modified by both types of plasma sources was observed. The peel strength of the PA-12 sample modified by DCSBD for 5 s increased to 0.0461 N mm⁻¹, which is more than 7 times
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higher than compared to the peel strength of untreated PA-12 (0.006 N mm$^{-1}$). After a 10 s DCSBD treatment the peel strength was increased 12 times and reached a value of 0.07145 N mm$^{-1}$. The peel strength of PA-12 that was modified by a 15 s DCSBD treatment remained almost at the same value with only a slight decrease (0.0575 N mm$^{-1}$). The modification of PA-12 by an industrial corona was less efficient for the 5 and 10 s treatment times, and for the 15 s treatment time the peel strength was increased to 0.0614 N mm$^{-1}$. It is evident that diffuse plasma of DCSBD is more efficient in obtaining the better adhesion of the PA-12 foils with short treatment times. Fig. 4 demonstrates that the same peel strength as was obtained for PA-12 by DCSBD at treatment time 10 s compared with the treatment by the industrial corona for 15 s. The efficiency of DCSBD plasma from the adhesion modification point of view should be verified by measuring the peel test at different times after treatment to investigate ageing effect as it was done in the case of wettability.

3.3 XPS analysis

XPS analysis was performed in order to explain the observed changes in adhesion and wettability of the PA-12 foils. The XPS survey spectra for the untreated and plasma treated PA-12 foils for DCSBD and industrial corona plasma sources showed the peaks at 285 eV, 400 eV and 532 eV correspond to the C 1s, N 1s and O 1s, respectively. The atomic concentration of these elements and the atomic ratios of O/C and N/C are summarized in Table 1.

As a result of the plasma treatment, the concentration of the individual chemical elements changed. The DCSBD plasma treatment influenced the concentration of oxygen and carbon on the surface of the foil. Compared to the untreated sample, the concentration of both elements increased. In the case of the 15 s treatment time, the O/C ratio was 71.4%, whereas for the untreated, the O/C ratio was 40.6%. A similar trend was observed for the N/C ratios.

Compared to the DCSBD plasma treatment, the industrial corona plasma treatment did not affect the atomic composition as much. For the 15 s treatment time, the O/C ratio reached only 50.8%. On the other hand, the N/C ratio reached 79%, which was approximately 2 times higher compared to untreated foil.

For both sources, an examination of the ageing behavior showed similar decreasing trends, however the O/C ratio obtained for DCSBD seems to be more promising and indicates that this type of plasma treatment is chemically more stable.

The peak fitting routines were done in order to evaluate the changes in the bond structure. The high resolution C 1s peak was fit with 5 principal components: C-C (binding energy at 284.8 eV), C-N (285.6 eV), C-O (286.3 eV), NH-C=O (287.9 eV) and O-C=O (289.0 eV), as shown in Fig. 5. The results of the fits are presented in Table 2. After the DCSBD plasma treatment, an increase of the components which combine C and O, the most significant is C-OH along with a decrease of the C-N and C/C=O components were observed. In this context, NH-C=O component seems to be stable and is not affected by plasma. These observations were more visible for the DCSBD plasma treatment.

The results corresponding to corona treatment indicate that this type of treatment is not as effective and the bond modification is modest. Similar behavior was observed for ageing experiments.
Table 1: XPS elemental analysis of the untreated and plasma treated PA-12 foils.

| sample                  | Chemical composition (%) | Atomic ratio (%) |
|-------------------------|--------------------------|------------------|
|                         | Treatment time (s)/ Ageing (days) | C   | O   | N   | O/C | N/C |
| untreated               | --                       | 69  | 28  | 3   | 40.6| 4.3 |
| Plasma treated DCSBD    | 5                        | 59  | 38  | 3   | 64.4| 5.1 |
|                         | 10                       | 60  | 36  | 4   | 60.0| 6.7 |
|                         | 15                       | 56  | 40  | 4   | 71.4| 7.1 |
| Plasma treated corona   | 5                        | 64  | 31  | 5   | 48.4| 7.8 |
|                         | 10                       | 62  | 33  | 5   | 53.2| 8.1 |
|                         | 15                       | 63  | 32  | 5   | 50.8| 7.9 |
| Ageing DCSBD (5s plasma treatment) | 1                        | 61  | 36  | 3   | 59.0| 4.9 |
|                         | 5                        | 57  | 40  | 3   | 70.2| 5.3 |
|                         | 14                       | 63  | 33  | 4   | 52.4| 6.3 |
| Ageing corona (5s plasma treatment) | 1                        | 71  | 25  | 4   | 35.2| 5.6 |
|                         | 5                        | 71  | 25  | 4   | 35.2| 5.6 |
|                         | 14                       | 68  | 28  | 4   | 41.2| 5.9 |

Table 2: Deconvolution analysis of C 1s peaks of untreated and plasma treated PA-12 foils.

| Relative area corresponding to different chemical bonds (%) |
|-----------------------------------------------------------|
| sample                  | Treatment time (s)/ Ageing (days) | C-C/ C-H (284.8 eV) | C-N (285.6 eV) | C-O (285.3 eV) | NH-C=O (287.9 eV) | O-C=O (289.0 eV) |
|-------------------------|-----------------------------------|----------------------|----------------|----------------|-------------------|-------------------|
| untreated               | --                                | 54                   | 20             | 9              | 10                | 7                 |
| Plasma treated DCSBD    | 5                                 | 44                   | 13             | 22             | 11                | 10                |
|                         | 10                                | 54                   | 4              | 23             | 12                | 7                 |
|                         | 15                                | 47                   | 13             | 18             | 12                | 10                |
| Plasma treated corona   | 5                                 | 53                   | 16             | 13             | 11                | 7                 |
|                         | 10                                | 50                   | 17             | 13             | 11                | 9                 |
|                         | 15                                | 50                   | 16             | 12             | 12                | 10                |
| Ageing DCSBD (5s plasma treatment) | 1                        | 52                   | 7              | 22             | 12                | 7                 |
|                         | 5                                 | 53                   | 7              | 22             | 10                | 8                 |
|                         | 14                                | 54                   | 7              | 23             | 10                | 6                 |
| Ageing Corona (5s plasma treatment) | 1                        | 56                   | 18             | 11             | 9                 | 6                 |
|                         | 5                                 | 53                   | 21             | 14             | 8                 | 4                 |
|                         | 14                                | 52                   | 19             | 14             | 9                 | 6                 |
4 Conclusions

This work investigated the effect of atmospheric pressure plasma treatment on PA-12 foil. The plasma sources tested were DCSBD and industrial corona. The reported results show a significant increase in wettability of the samples. The plasma treatment of polyamide has been demonstrated to be efficient and thus is very convenient for in-line processing. The adhesion measurements proved that the adhesive properties were positively influenced by the plasma modification. The XPS testing proved to be a very effective method for the examination of the chemical changes on the PA-12 surfaces. Using XPS, the introduction of the oxygen containing groups on the PA-12 surface was confirmed. The attention was also devoted to the ageing of the plasma treatment. Contact angle measurements and XPS results showed no significant changes in wettability with these results confirmed after 14 days of ageing. According to the results we can conclude that DCSBD is a more efficient plasma source for the modification of PA-12 foils than an industrial corona. The differences in surface modification between diffuse plasma of DCSBD and filamentary plasma of industrial corona are related to their discharge properties because a more active species can interact with the surface in the case of DCSBD treatment due to the evenly distributed plasma.

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