The impact of DCSBD plasma discharge on polypropylene

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Abstract. The diffuse coplanar surface barrier plasma discharge (DCSBD) still belongs to specific methods of modifying (activating) the surface of polymeric materials. The present work deals with surface treatment of polypropylene foils by plasma discharge, investigation and subsequent identification of changes caused by mentioned discharge. The modified surface was examined by measuring the wetting angle. Film surface morphology and topography was investigated by scanning electron microscope (SEM) and atomic force microscopy (AFM), respectively. Subsequently, it was examined whether the modification of polypropylene by DCSBD plasma discharge only affects the surface of the investigated material or also changes structural properties in studied material, based on the obtained data from DMA analysis.

1. Introduction

The plasma discharge surface treatment of polymeric materials can be realized on various technical devices [1–3]. Plasma reactor KPR 200 mm based on DCSBD for continuous two-sided surface treatment of flat polymeric materials of thin textiles and cords by plasma, at the workplace of the Center for Quality Testing and Materials Diagnostics (CEDITEK), Faculty of Industrial Technology in Púchov. The KPR 200 mm plasma reactor in its unique design artfully utilizes the workspace of the line, where it is possible to work with DCSBD plasma discharge (Diffuse Coplanar Barrier Discharge) a.) In the use of planar electrodes; b) by machining on concave curved electrodes – continuous machining of materials preferably in wrapping – foils, textiles, etc. This work provides trivial information about the possibilities of using DCSBD plasma discharge on a laboratory line for polymer materials treatment – plasma reactor KPR 200 mm.

The subject of research of several expert works is either setting of suitable power of electrodes, time suitable for optimal modification, or distance of sample from electrode surface. Research results and surface modification quality are often monitored by: aging effects – measuring the wetting angle of liquids and determining the surface energy; formation of polar oxygen groups – FTIR infrared spectroscopy; topological changes using AFM microscopy, SEM microscopy, adhesion evaluation and XPS analysis. The resulting changes in the chemical and physical properties of the surface of materials after modification by DCSBD by plasma discharge are often desirable for industrial practice conditions – for example in printing techniques – suppressibility; surface modification resistance – aging. It is important to note that the DCSBD plasma discharge is generated under atmospheric conditions on the KPR 200. The materials that are modified by the DCSBD plasma discharge are: thermoplastics, glass [4], paper [5], various fibers [6–8] and textiles [9, 10] include materials in medical sphere [11, 12] and electrotechnics [13]. The need to use secondary raw materials in the plastics industry is urgent when generating large amounts of new plastic waste. In the Atlas of Environmental Remediation Methods,
Water Remediation Methods, Induced Gas Flotation (IGF) [14] flotation is mentioned as a method where the key flotation process takes place at the boundary: material - air - water, using physical-chemical properties of materials and liquids (hydrophobicity of the material surface and surface tension). The Waste Management Magazine published in 2015 [15] provides widespread information on the separation of plastic waste (PE – polyethylene, PP – polypropylene, PVC – polyvinyl chloride, PET – polyethylene terephthalate, PUR – polyurethane and others) through the flotation process. Of the abovementioned wastes / materials, thermoplastics include: PE, PP, PVC, PET, PS, EPS and thermosets include polyurethane (PUR).

2. Materials and methods

The polypropylene samples are of the solid packaging material used. The sample sizes were approximately: 25 mm × 10 mm × 0.4 mm.

Surface modification of samples was performed on planar electrode. DCSBD plasma discharge was set on control panel at value 350 W, time 45 s, distance from electrode: 0.15–0.18 mm.

Dynamic mechanical analysis (DMA) was performed by DMA Q800 thermal analysis device from the manufacturer TA Instruments. The TA Instruments Q800 Dynamic Mechanical Analyzer (DMA) is a thermal analytical instrument used to test the mechanical properties of many (different) materials. Dynamic-mechanical analysis was performed on standard polypropylene and polypropylene with DCSBD plasma discharge at three different frequencies: 0.1, 1 and 10 Hz (figure 1). Modules that were measured and compared: storage module ($E'$), loss modulus ($E''$), and loss angle – tan $\delta$. Experimental conditions have been set as follows: Module – DMA Multi-Frequency – Strain, Clamp Tension: Film, Method Temperature Ramp, dimensions of sample 15–17 mm × 7 mm × 0.4 mm; temperature range: -35 to 35 °C, heating rate of 3 °C min$^{-1}$, frequencies: 0.1, 1 and 10 Hz. The measurement records were read in TA Universal Analysis 2000, then the measurement values were exported from the software and processed in Microsoft Office 365 – Excel.

For study of surface morphology, the NT-206 atomic surface microscope (AFM), operating at the contact mode under the laboratory conditions with tip force constant of 0.95 N m$^{-1}$, was used. The 16 × 16 μm images at various places of sample were obtained and evaluated in the Surface Xplorer 1.0.8.65 software.

Changes in the surface of the experimental material induced by its modification by DCSBD plasma discharge were monitored using a Tescan Vega 3 thermo-emission scanning electron microscope (SEM).

The sessile drop is the standard arrangement for optical measurement of the wetting angle using CCD camera and MATLAB software. UEye software was used to capture the drop profile.

![Figure 1. Polypropylene sample modified by DCSBD plasma discharge in DMA analyser.](image-url)
3. Results and discussion

Storage modulus values are similar to plasma discharge before and after DCSBD surface modification (figure 2). The graphs show the decreasing trend of the elastic module at three frequencies of 0.1, 1 and 10 Hz in the temperature range of -20 to 30 °C, which is the temperature interval for polypropylene storage. The values of the storage modulus of polypropylene before and after modification by DCSBD by plasma discharge are only slightly different for each of the measured frequencies, located close together.

![Figure 2. Storage module of PP before and after DCSBD discharge application.](image)

The loss modulus values of polypropylene before and after modification by DCSBD discharge are significant different. The curves on figure 3 show the decreasing trend of the loss modulus at three frequencies of 0.1, 1 and 10 Hz in the temperature range of -20 to 30 °C. The values of loss modulus after DCSBD discharge showed decreasing character compare to standard polypropylene (at all three used frequencies).

![Figure 3. Loss modulus of PP before and after DCSBD discharge application.](image)

The figure 4 shows the resulting values of loss angle tan δ of samples of polypropylene and polypropylene with DCSBD surface treatment by plasma at different frequencies.
If the tan $\delta$ value is higher, the viscous component dominates. Otherwise, if the tan $\delta$ value is lower, it is a more elastic material. Therefore, we can confirm that lower tan $\delta$ values show samples that have been modified by DCSBD plasma discharge. The values remained unchanged at the lowest frequency.

The surface of standard (reference) polypropylene without plasma (DCSBD) modification can be evaluated as practically homogeneous, with almost no significant differences in height and surface formations, and it can be caused by manipulation during material/sample preparation or utilization. Practically homogeneous surface of polypropylene without plasma modification was observed at various surface places by SEM (figure 5) as well as AFM (figure 6).
Significant changes from the standard PP can be observed on the surface of polypropylene sample modified by plasma discharge (DCSBD). The DCSBD plasma discharge caused that the surface has many new features that are significant in height and thus more rugged. The evident change in surface morphology of the PP sample after modification by plasma discharge can be seen in the figures 7 and 8. According to AFM measurements, the height of unevenness (formations) on the plasma modified surface was increased almost four times in comparison to non-modified surface.

Figure 6. Morphology of standard polypropylene (without DCSBD plasma modification).

Figure 7. SEM images of polypropylene after DCSBD plasma modification.

Figure 8. Morphology of polypropylene after DCSBD plasma modification.
The wetting angle of diiodomethane and distilled water on the polypropylene surface was changed in the expected way; with small standard deviations which could be caused by an uneven layer of modification or imperfections of the modified polypropylene surfaces. However, the wetting angles after DCSBD plasma modification varied minimally (figure 9).

![Image showing wetting angles](image_url)

**Figure 9.** The change of wetting angle of distilled water and diiodomethane on the surface of standard polypropylene and polypropylene modified with DCSBD plasma discharge.

Indeed, the surfaces of the thermoplastic under investigation are altered after the plasma discharge has been applied, as evidenced in particular by the AFM and SEM microscopy methods, while the wetting angle results indicate that the plasma process needs to be fine-tuned because the changes of wetting angles are minimal. It may be necessary to make changes to the ceramic electrode power settings, sample-to-electrode distance, DCSBD exposure time to plasma discharge etc.

### 4. Conclusions

The aim of the present work was to study selected thermoplastic from packaging material that can serve as secondary raw material, comparing their surface properties before and after application by plasma DCSBD discharge. Two samples of polypropylene were used in the experiment: a standard sample and a plasma discharge treated sample (DCSBD) – their selected properties were compared. The surface modification of the samples was realized by diffusion coplanar barrier discharge (DCSBD) on the plasma reactor KPR 200. A suitable type of thermoplastic was selected (flat and thin) sample from the packaging material. The first conclusions can be drawn from the results achieved. Dynamic-mechanical analysis was performed on a sample of standard polypropylene and polypropylene with DCSBD plasma discharge at different frequencies and the elastic modulus ($E'$), loss modulus ($E''$) and loss angle tan $\delta$ were evaluated and compared. Results indicate a change in DCSBD plasma discharge specimens. The course of the curves at selected modules and frequencies varies, which may be due to DCSBD plasma discharge, which has modified not only the surface but also the intrinsic properties of polypropylene.
The surface modification of polypropylene is confirmed also by SEM and AFM microscopy results, when the polypropylene surfaces after plasma treatment were significantly more segmented with new formations. However, the changes in wetting angle of wetting liquids on plasma modified surfaces are minimal.

The DCSBD plasma discharge can be used to modify/treat the surfaces of used thermoplastics to better separate the recycling of secondary raw materials by flotation.

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