Contact angle analysis of corona treated polypropylene films

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Abstract. In this work, the effect of the surface modification of polypropylene films via corona treatment was investigated. Polypropylene films were treated with negative and positive corona discharge, at atmospheric pressure, for 5 minutes, at two different temperatures - 25 °C and 90 °C. The changes in the surface free energy were investigated by means of contact angle measurements. The Bickerman’s method was applied to determine the polar and dispersion components of the polymer surface free energy, on the basis of the theory of Owens, Wendt, Kaelble and Uy. Atomic force microscopy was used to analyze the polymer surface morphology changes of the films with temperature. According to the findings, in all cases the corona treatment increases the surface free energy of polypropylene films and its polar part, in comparison with the untreated samples. The effects of negative and positive corona polarities display some specific features which could be associated with different charged group introduced onto the film surface during the corona treatment. The total final effect depends on the simultaneous action of the two competing factors - temperature and corona polarity. The most pronounced effect was observed for high temperature negative corona treatment.

1. Introduction
Polypropylene (PP) is one of the most widely used polymers owing to its high transparency, small weight, thermal stability, chemical resistance, easiness to manufacture, and low cost [1, 2]. However, PP is known to be non-polar, low surface energy material, and its hydrophobic characteristics cause poor wettability. The wettability is very important characteristic for many industrial applications of PP films, for example, ink printing, paints and coatings, lamination and conventional adhesives, composites preparation [1, 2].

Different techniques, such as plasma, ultraviolet irradiation, and electron bombardment treatments have been used to overcome these problems by modifying the surface properties [1, 3-6]. Another possible technique for surface modification of polymers is corona discharge [1, 7]. Atmospheric-pressure corona discharge is very attractive for various industrial applications because of its relatively low-cost, in-line treatment, good process control, high speed, operation without vacuum, and independence of the shape of the parts. The ability to change the surface properties of the most
external layers of the material without modifying its bulk characteristics is also an advantage. Hence, one can improve the adhesion without any loss of the good mechanical properties.

When polymers are subjected to corona discharge in air, various ion groups initiated by the corona are injected into sample surface, enhancing the concentration of polar groups on it [1, 7-9]. The process leads to surface free energy increase. The type of the inserted groups could be governed by changing the corona type, temperature, air humidity and others factors [8, 10, 11]. However, systematic studies on the influence of corona discharge conditions, and especially of the corona polarity, on surface modification are still lacking.

In the present paper, the effect of corona discharge polarity and temperature on the surface modification of PP films was investigated. The changes in the polar, $\gamma_s^p$, and dispersion, $\gamma_s^d$, components of surface free energy were used as a measure of the degree of surface modification. The Bickerman’s method [12] for precise measurements of contact angles of very small liquid sessile drops in contact with substrates was used to determine $\gamma_s^p$ and $\gamma_s^d$ on the basis of the theory of Owens, Wendt, Kaelble and Uy [13, 14].

2. Materials and methods

2.1. Sample preparation

Isotactic polypropylene (i-PP) films with thickness of 20 μm were supplied from “Assenova Krepost” LTD, Bulgaria. The films were used as received. They were cleaned with alcohol in an ultrasonic bath for four minutes, washed in distilled water, and dried on filter paper under room conditions. Samples with dimension (3 × 3) cm² were cut from the cleaned films.

2.2. Corona treatment

The samples corona treatment was carried out in a point-to-plane three-electrode corona discharge system [15]. The experimental scheme, presented in figure 1, consists of a corona electrode (needle), a grounded plate electrode, and a metal grid placed between them. Introducing a grid between the corona electrode and sample limits the sample surface potential to that of the grid and produces more uniform distribution of the charge on the sample surface. The distance between the grounded plate electrode and the grid was 10 mm and the distance from the grid to the corona electrode was 7 mm. A voltage of ± 5 kV was applied to the corona electrode and 1 kV with the same polarity, as that of the corona electrode, to the grid. The corona discharge system was placed into thermo chamber with...
temperature control so that the samples, placed on the grounded plate electrode, were charged in positive or negative corona for 5 minutes, at two different temperatures (25 °C and 90 °C).

2.3. Morphology

i-PP surface morphology was investigated by means of Atomic force microscope (AFM NANOSURF FlexAFM). The samples were scanned with a standard silicon cantilever (type Tap 190Al-G) and the measurements were performed in ambient atmosphere, and dynamic operating mode. The applied force was always minimized, not to deform the samples. The surface topographic images of the films before and after temperature treatment were taken.

2.4. Contact angle measurements

For the measurements of the contact angle, $\theta$, drops from distilled water and diiodomethane with varying volume were inserted onto the solid i-PP film surface, at room temperature, using a precise 10 μl micro syringe (Innovative Labor System GmbH, Germany) supplied with steel needle. The drop volume was from 2 μl to 6 μl. The drop diameters were measured with optical microscope (MBC-9, USSR) provided with a micrometer scale eyepiece. For each drop volume, and each testing liquid, 5 measurements were performed at different places onto the sample surface. The same procedure was repeated with six different samples. The final value of the contact angle is the mean value of the six samples measurements. The estimated error was less than 5 %.

Bickerman’s method [4, 12], in which the effect of gravity distortion is negligible and the drop may be considered as a segment of a sphere, was applied to derive the contact angle:

$$\frac{d^3}{V} = \frac{24\sin^3 \theta}{\pi(2 - 3\cos \theta + \cos^3 \theta)}$$

where $V$ is the drop volume, and $d$ is the drop diameter.

Contact angle formation between a liquid drop and solid surface is presented in figure 2. The contact angle depends on the energies at the interfaces: solid-liquid ($\gamma_{sl}$), solid-vapor ($\gamma_{sv}$), and liquid-vapor ($\gamma_{lv}$). The symbols $\gamma$ with two indices describe the surface energy between the two phases in contact.

Following the theory of Owens and Wendt [13], and Kaelble and Uy [14], the surface free energy of a solid, $\gamma_s$, can be expressed as a sum of contributions from $\gamma^d_s$ and $\gamma^p_s$ components. Both can be determined from the contact angle data of polar and non-polar liquids with known dispersion, $\gamma^d_{lv}$, and polar, $\gamma^p_{lv}$, parts of their interfacial energy:

$$\gamma_s(1 + \cos \theta) = 2\left(\gamma^d_s \gamma^d_{lv}\right)^{1/2} + 2\left(\gamma^p_s \gamma^p_{lv}\right)^{1/2}$$
where $\gamma_{lv} = \gamma_{lv}^p + \gamma_{lv}^d$.

3. Results and Discussion

In order to distinguish the effect of high temperature treatment from corona discharge, a preliminary AFM study of surface morphology was performed. As it is seen in figure 3, the morphology is insignificantly altered by the temperature increase. The difference between the lowest and the highest surface points is $\Delta h = 52.3 \text{ nm}$ at $25 ^\circ\text{C}$ and it displays minor change after temperature treatment at $90 ^\circ\text{C}$ ($\Delta h = 55.4 \text{ nm}$). The results indicate that the degree of mechanical interlocking remains the same and this mechanism does not play role in the adhesive properties increase. It has been already shown that the corona treatment provokes formation of nano- to micron-sided globular mounds but it does not alter the film surface roughness [7-9].

![AFM images of 20 µm thick i-PP films, stored at room temperature (T = 25 ºC), and after annealing at T=90 ºC for 5 min.](image)

The investigated samples were divided into three main groups – uncharged, positively charged, and negatively charged. In each group, two different series were prepared with different temperature treatment (25 ºC and 90 ºC). The obtained values of the distilled water, $\theta^w$, and diiodomethane, $\theta^{DIM}$, contact angles, $\gamma_s$ of the films, and polarity ($P = \gamma_s^p / (\gamma_s^p + \gamma_s^d)$) are given in table 1.

| Sample type       | $T$ (ºC) | $\theta^w$ (deg) | $\theta^{DIM}$ (deg) | $\gamma_s$ (mJ.m$^{-2}$) | $P$  |
|-------------------|----------|-----------------|-----------------------|------------------------|------|
| Uncharged         | 25       | 97.0 ± 0.8      | 56.9 ± 0.9            | 30.4                   | 0.03 |
|                   | 90       | 100.4 ± 0.5     | 61.4 ± 0.6            | 27.8                   | 0.02 |
| Positively charged| 25       | 90.5 ± 0.8      | 49.4 ± 0.1            | 32.3                   | 0.05 |
|                   | 90       | 91.0 ± 2.0      | 50.4 ± 0.7            | 34.2                   | 0.05 |
| Negatively charged| 25       | 95.1 ± 0.7      | 56.6 ± 0.9            | 30.6                   | 0.04 |
|                   | 90       | 90.0 ± 2.0      | 57.0 ± 3.0            | 30.3                   | 0.12 |

The temperature treatment alone leads to an increase in the contact angles for both liquids and the corresponding decrease in the surface free energy. This effect could be explained by thermal annealing, where gradual structural change from smectic to monoclinic crystal structure takes place simultaneously with formation of a thin surface layer of low-molecular-weight compounds of i-PP [1].
For both experimental temperatures, $\theta^\circ$ decreases after the corona treatment and correspondingly the $\gamma_s^d$ increases for both corona polarities, in agreement with the results of Cáceres at al. for negative corona treatment [16]. The values of $\gamma_s^p$ and $\gamma_s^d$, depending on the treatment conditions, are shown in figure 4. As it can be seen, the changes in surface free energy of the corona treated samples are due to the increase of $\gamma_s^p$, leading further to enhanced polarity. The findings can be explained by introduction of oxygen containing polar groups such as hydroxyl, peroxy, hydroperoxide, carbonyl, carboxylic, carbonate, and ester onto the sample surface during the corona treatment [7, 8, 17, 18]. Our results (see table 1 and figure 4) indicate that the negative and positive corona polarities treatments display different specific features which could be explained by different kinds of polar groups, created during the corona treatment. Yovcheva at al. [19] based on X-ray photoelectron spectroscopy analysis, have found that the oxygen content differs in samples charged in different corona polarity, leading to the formation of different surface local levels. In negative corona polarity, where the most important ions are the $\text{CO}_3^-$, the electric field stimulates introduction of oxygen ions or oxygen-containing groups onto polymer surface. In positive corona polarity, where the prevailing ions are $\text{H}_n\text{O}_m\text{H}^+$ type, the electric field stimulates desorption of oxygen atoms from the surface. The presence of two different processes, oxygen adsorption and desorption during the sample charging, are most probably stimulated in different ways and/or have different rates in the positive and negative corona. The lower oxygen content in positively charged samples in comparison to the negatively charged samples [19] could explain the higher values of $\gamma_s^d$ obtained for positive corona treated samples.

The observed changes of the surface energy are result for the interplay of the two simultaneously acting and competing effects: temperature and corona polarity. In general, the temperature increase leads to a decrease in surface free energy, while the corona treatment stimulates the surface free energy increase. According to our results, the most pronounced effect of increase in the surface polarity was observed for high temperature negative corona treatment. Obviously further detailed studies are needed to reveal the exact impact of the simultaneous action of these factors - temperature and corona polarity.

4. Conclusion

The obtained results indicate that corona discharge, applied in combination with high temperature leads to a decrease in the water contact angle, an increase of surface polarity, and consequently leads to an improved weatability of the films. The effect is observed for both corona polarities. The observations are believed to be due to introduction of different oxygen containing polar groups, such
as hydroxyl, peroxy, hydroperoxide, carbonyl, carboxylic, carbonate, and ester onto the i-PP surface. Negative and positive corona polarities treatments display some specific features. The strongest increase in the surface polarity was observed for negative corona high temperature treatment. The differences in the results for both polarities could be associated with different type and amount of the charged group injected into the polymer surface during the corona treatment. The results show that the effect of the treatment was dependent on the simultaneous action of two treatment factors - temperature and corona polarity.

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