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# Wettability of Polymeric Materials after Dielectric Barrier Discharge Atmospheric-pressure Plasma Jet Treatment

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Wettability is an important feature in describing the physicochemical surface properties of material surfaces. It can be determined by measurements of the contact angle. A plasma jet reactor with dielectric barrier discharge (DBD) was used to modify the contact angle of selected polymeric materials.

## 1. Introduction

Acrylonitrile-butadiene-styrene (ABS), polypropylene homopolymer (PP-H), and high-impact polystyrene (HIPS) are important and widely used polymeric materials that are characterized by different mechanical and thermal properties. The positive qualities of these materials include the ease of heat and mechanical processing and high chemical resistance. Thus, ABS, PP-H, and HIPS are used in many technological fields, such as construction engineering, the food industry, and car manufacturing.[1,2]

One feature of such materials is their wettability. It is important, for example, in food packaging, self-cleaning, water repellency, inks and superhydrophobic coatings, injection of medical polymers, and particle attraction in deoxyribonucleic acid (DNA) purification.[3,4]

One method of determining this parameter is to measure the contact angle. The material is referred to as hydrophobic when the contact angle formed between a solid flat surface of the material and the tangential plane of the liquid drop surface $\theta > 90°$. If $\theta < 90°$,[5,6] this material is referred to as hydrophilic (Fig. 1).

By appropriate treatment (mechanical, thermal, or chemical), hydrophobic properties may be changed in accordance with the need. Mechanical modification methods cause loss of modified material as production waste and chemical methods often involve the application of toxic compounds, increasing the environmental burden. Thermal methods cannot be applied for all materials, especially non-heat-resistant ones, as heat may affect the internal structure of the sample. One of the methods used to convert these properties, is the use of nonthermal plasma.[8–10]

Generally, because of the ease of chemical interaction, plasmas have found a variety of applications in many fields of science and technology.[11–17] The use of a plasma reactor with

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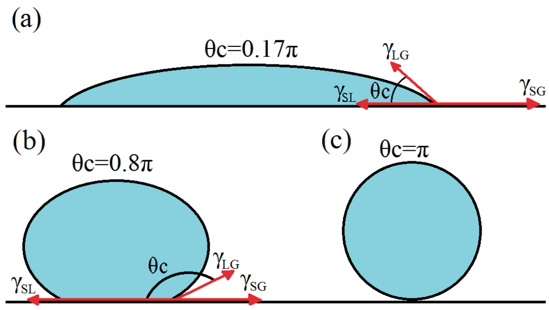


Fig. 1. (Color online) (a) Good wetting, (b) poor wetting, and (c) complete lack of wetting.(7)

barrier discharge is most common in the technological treatment of drinking water, where ozone generated in discharges replaces toxic chlorine. Applications of dielectric barrier discharge (DBD) reactors include decontamination of water, gas, and soil. It may also be used for the decontamination of surfaces, containers, medical instruments, and tissues and to enhance healing.(18–22)

We examine the effectiveness of plasma treatment on ABS, HIPS, and PP-H using a plasma jet reactor with DBD. Many types of reactors were tested,(23–25) but the advantage of our reactor working at atmospheric pressure is its compact size, low energy consumption, operation simplicity, and safety as temperature is relatively low and the gases used are nontoxic and do not cause secondary pollution. The operation spot is small and controllable, ensuring high flexibility and precision of the device, which is especially important for biotechnological samples.

## 2. Experimental Method

A plasma jet reactor (Fig. 2), supplied with a voltage of 3.7 kV at a frequency of 17 kHz and input power of 9.5 W was used to study the properties of materials treated with nonthermal plasma. The distance between the plasma jet and the sample was 20 mm. The treatment times were 10, 30, 60, 90, and 120 s.

All tested samples were 30 × 40 mm$^2$ with a thickness of 2 mm. The gas temperature was lower than the softening temperature of the material with the lowest thermal resistance for all measurements. The tests were performed in triplicate for five samples made of each of the tested materials for each time, gas mixture, and flow rate. Relative humidity ranged from 59 to 64% and the temperature of ambient air was from 21 to 23 °C. Thermal parameters of the materials are shown in Table 1.

After applying plasma, all samples were placed in a specially prepared rack. The individual samples were wetted with 10 μl of distilled water using an automatic pipette. After wetting, photographs of the sample were taken using a camera mounted on the same rack.

Angle measurements were performed for each drop using graphics processing software. Figure 3(a) illustrates the process of plasma treatment on the HIPS material, and Fig. 3(b) shows the sequence of applying a drop of distilled water during the measurement of contact angle on the sample.

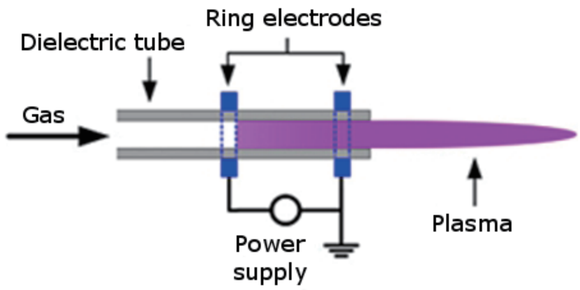


Fig. 2. (Color online) DBD reactor with two ring electrodes on a ceramic tube.

Table 1
Properties of materials.[26]

| Name | Softening temperature (°C) | Reference contact angle (°) |
|---|---|---|
| HIPS | >90 | 90 |
| ABS | >94 | 75 |
| PP-H | 95 | 82 |

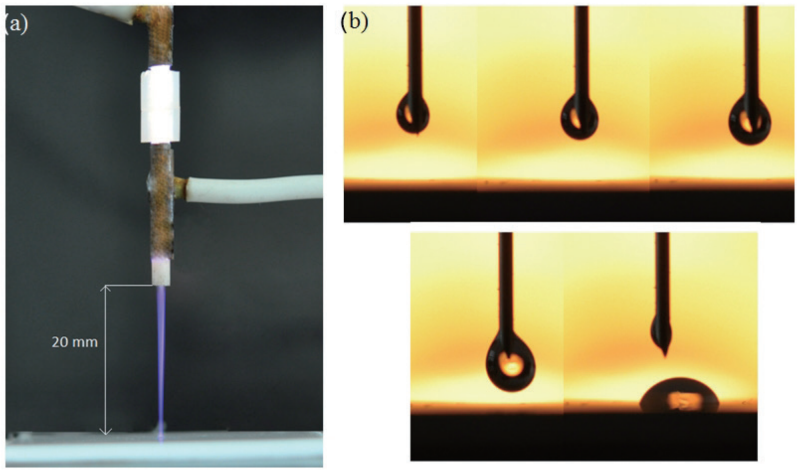


Fig. 3. (Color online) (a) Image of treating a sample of HIPS material and (b) sequence of applying a drop to measure the wetting angle.

## 3. Results and Discussion

Measurements of wettability were performed for samples of ABS, HIPS, and PP-H. Figure 4 shows contact angles for PP-H as a function of the amount of air added. The length of time of plasma exposure on the surface of the sample was 30 s. The contact angle of the control sample was 82°. The impact of the plasma on the surface decreased the contact angle. The change in the flow of air had no significant effect.

The contact angle for ABS (control angle of 75°) is shown in Fig. 5. It can be seen that, owing to the action of plasma, the contact angle decreased. Similar results for the plasma treatment of this material were observed as the flow rate of helium was increased (from 1.17 to 1.5 l/min).

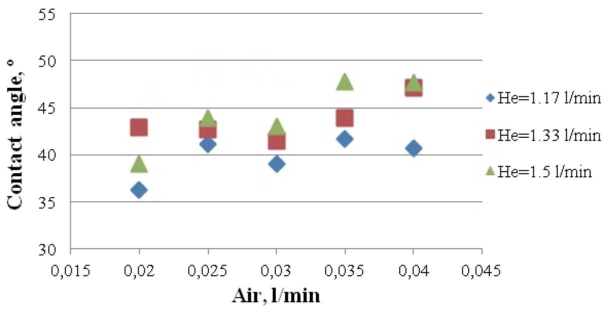


Fig. 4. (Color online) Surface contact angle of PP-H; duration of plasma treatment: 30 s.

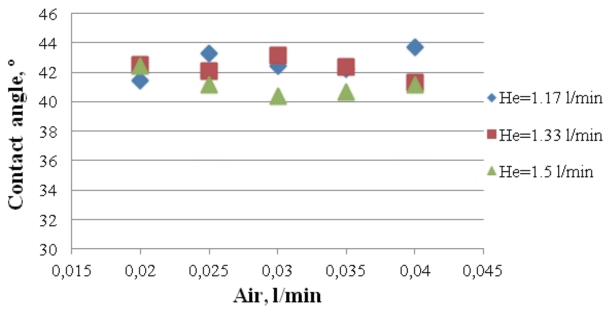


Fig. 5. (Color online) Surface contact angle of ABS; duration of plasma treatment: 30 s.

The contact angle for the control sample of HIPS was 90°. During the plasma treatment, a slightly increasing trend of contact angle with increasing air flow fraction can be observed in Fig. 6.

Figure 7 shows the contact angles of the three materials treated with plasma jet for 120 s. The smallest contact angles were achieved for HIPS and the greatest, for PP-H. In this case, a slight increase in angle with increasing amount of air added was observed.

Figure 8 shows the contact angles against the duration of plasma exposure at constant flow rates (helium: 1.33 l/min; air: 0.03 l/min). The change in the plasma exposure time had no significant effect on the contact angle.

Figure 9 shows the contact angle as a function of time elapsed from the end of plasma treatment on polymeric materials. The longer the time from the end of the treatment, the closer the contact angle of the material approaches the initial measured value.

According to the obtained results, the major factor influencing the treatment process for all tested materials was gas composition. The overall gas flow rate did not play a crucial role in surface treatment. Plasma burning in ambient air enabled the formation of highly reactive oxidative compounds, such as singlet oxygen, hydroxyl radicals, and ozone, even with the DBD APPJ working with pure helium. However, as indicated in Figs. 4, 6, and 7, the addition of air to the substrate gas contributed to the higher concentration of generated oxidants and to the improvement of the hydrophilic properties of the surface. Gas composition prevailed even on treatment time, because the surface contact angle was significantly reduced even after very short 5 s treatment and longer treatment time caused only slight changes in its final contact angle value, as shown in Fig. 8. Plasma treatment effects depended on the chemical composition of the sample; however, they were clearly visible for all treated materials. Contact angle could be reduced from 90 to 16°, from 75 to 32°, and from 82 to 36° for HIPS, ABS, and PP-H, respectively. The repeatability of experiments was good; average errors did not exceed 9%. However, the tendency of contact angle reduction is comparable for all three materials, the highest reduction took place for HIPS. All tested materials have shown a tendency to have increased contact angle with time from the treatment process, as well. The biggest change was also observed for HIPS (Fig. 9), which is a multiphase structure with polybutadiene as the rubber dispersed phase incorporated in the styrenic rigid matrix. As an effect of mild surface

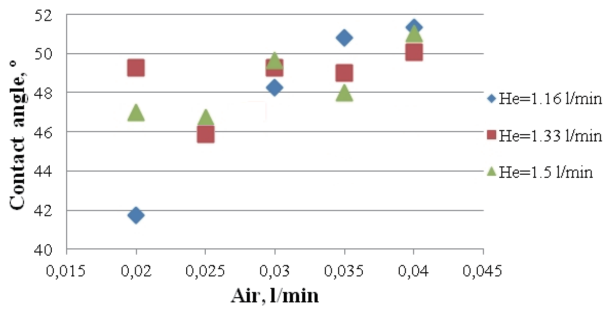


Fig. 6. (Color online) Surface contact angle of HIPS; duration of plasma treatment: 30 s.

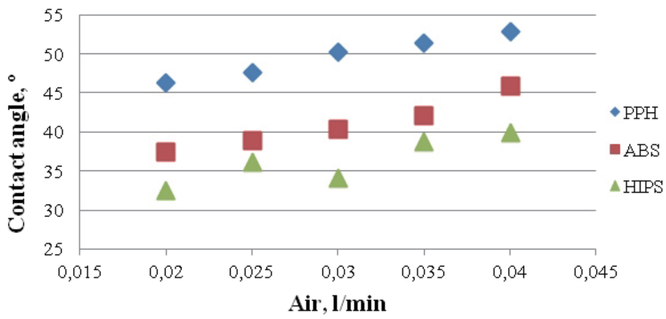


Fig. 7. (Color online) Surface contact angle for different materials as a function of air flow. Plasma treatment time, 120 s, helium flow rate, 1.33 l/min.

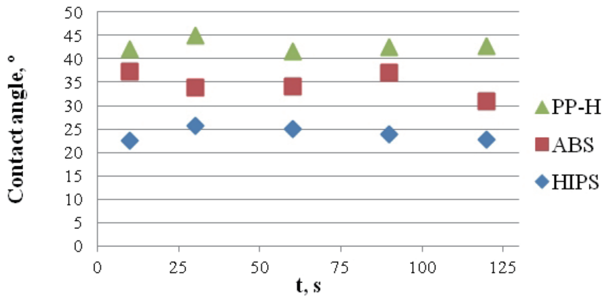


Fig. 8. (Color online) Surface contact angle as a function of the duration of plasma treatment. He = 1.33 l/min and air = 0.03 l/min.

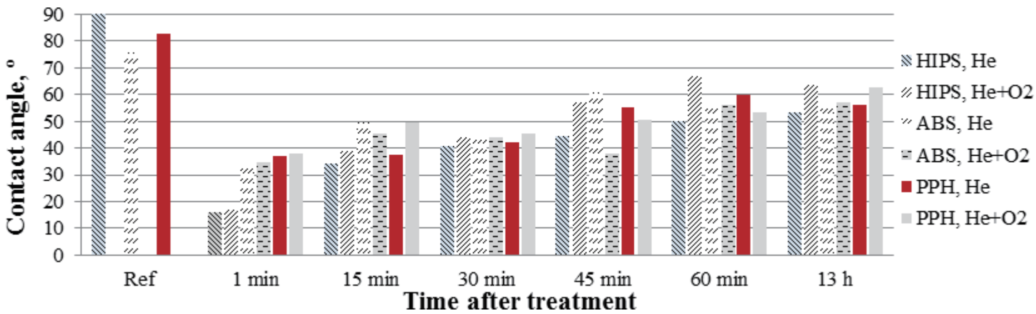


Fig. 9. (Color online) Dependence of surface contact angle on time elapsed since plasma treatment.

oxidation, one can expect the consumption of unsaturated chemical groups and the formation of oxidated moieties via free radicals and hydroperoxide formation. As the recovery rate was quite fast, the formation of stable cross-linked structures, damage to the polymeric chains, and degradation of materials did not take place.

The experiments were carried out in a semi-controlled atmosphere in the laboratory. No drastic effects of slight changes in relative humidity (from 59 to 64%) and temperature of ambient air (21 to 23 °C) on the plasma treatment process and obtained results were observed.

## 4. Conclusions

Exposure to nonthermal plasma generated in a barrier discharge reactor significantly reduced the hydrophobicity of materials, indicating its possible use in the modification of surface contact angles of materials used in technological processes. Results indicated that neither the gas flow rate increase nor the addition of air significantly affected these properties. The most important factor was the time since the completion of the treatment. Moreover, the observed recovery rate, indicates that the surface contact angle shows a tendency to increase with time after the treatment, but it does not attain the initial value.

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