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Influence of cold radiofrequency air and nitrogen plasmas treatment on wetting of polypropylene by the liquid epoxy resin

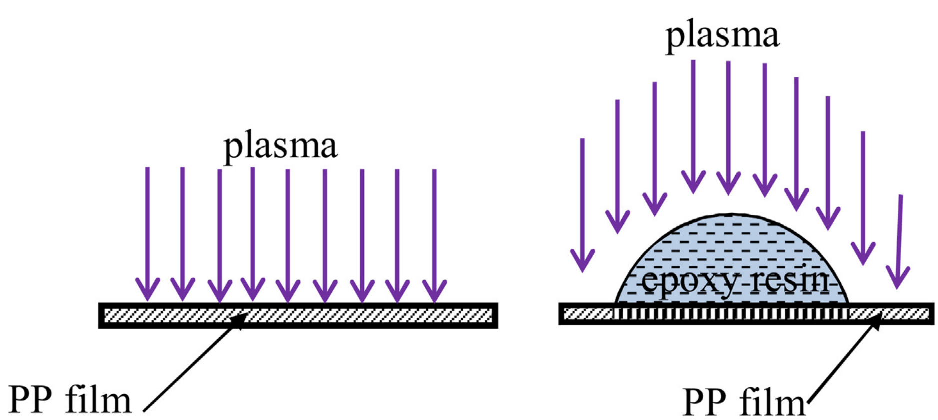
Edward Bormashenko[a,b,*], Barak Eldar[b], Gilad Chaniel[a], Victor Multanen[b], Gene Whyman[a]

[a] Ariel University, Faculty of Natural Sciences, Physics Department, 407000, P.O.B. 3, Ariel, Israel
[b] Ariel University, Chemical Engineering and Biotechnology Department, 40700, P.O.B. 3, Ariel, Israel

HIGHLIGHTS

- Polypropylene films and epoxy droplets were exposed to air and nitrogen plasmas.
- Solid/air and solid/liquid interfacial tensions were increased by plasma treatment.
- The solid/air interface tension was modified by plasmas stronger than the solid/liquid interface tension.
- The impact of the air and nitrogen cold plasma treatment on the contact angle hysteresis is reported.

GRAPHICAL ABSTRACT



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ABSTRACT

Plasma treatment increases the specific surface energy of condensed phases: solids and liquids. Impact of the radiofrequency air and nitrogen cold plasmas on the surface properties of the polypropylene film and liquid epoxy resin was investigated. Solid/air and solid/liquid interfacial tensions are increased by plasma treatment. The presented experiments enabled separation of the increase in the interfacial tensions due to the plasma irradiation. The solid/air interfacial tension was modified by oxygen and nitrogen plasmas stronger than the solid/liquid interfacial tension. The impact of the air and nitrogen cold plasma treatments on the contact angle hysteresis is reported.

1. Introduction

A diversity of technological applications calls for the modification of the surface properties of polymer materials. These applications include packaging, protective coatings, adhesives, textile, printing, etc. It was also demonstrated that plasma treatment

* Corresponding author at: Ariel University, Faculty of Natural Sciences, Physics Department, 407000, P.O.B. 3, Ariel, Israel.
E-mail address: edward@ariel.ac.il (E. Bormashenko).

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improves the biocompatibility of implant materials and enables controlling biofouling [1]. A common approach to tailoring surface properties of polymer materials is to expose them to plasma discharge to modify their surface chemistry [1–7]. Various kinds of discharges were applied for this purpose including the atmospheric [4] and low pressure plasma discharges [5].

The plasma treatment creates a complex mixture of surface functionalities, which influence surface physical and chemical properties; this results in a dramatic increase in the surface energy and consequent change in the wetting behaviour of the surface [8–17]. It was demonstrated that plasma treatment leads to the electrical charging of a polymer surface [18].

It was suggested that hydrophilization of organic surfaces by plasmas may be at least partially related to the re-orientation of hydrophilic moieties constituting organic molecules [16,17–20]. Oxidation of plasma-treated surfaces and removal of low-mass fragments present on organic surfaces also contribute to hydrophilization [21]. Much effort has been spent in understanding the interaction of plasmas with solid organic surfaces, whereas data related to plasma treatment of liquids are scarce [22–26].

An interest in plasma treatment of liquid organic surfaces arose due to various practical reasons, including the possibility of decontamination of liquids by plasmas [22–26] and microfluidics applications of these surfaces, stipulated by their extremely low contact angle hysteresis [27–33]. Quantification of the impact exerted by plasmas on liquid surfaces faces serious experimental challenges. Our paper focuses on the estimation of impact of the cold plasma treatment on the macroscopic wetting parameters of the epoxy resin.

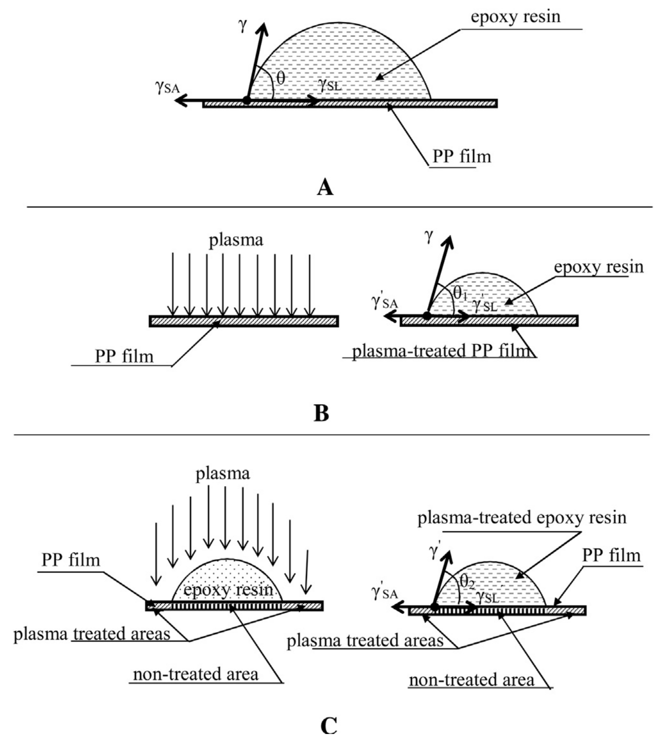

Fig. 1. Experiments performed for the establishment of the influence of plasma treatment on the wetting of PP surfaces by epoxy resin. A. Both liquid epoxy resin and PP substrate are untreated. B. Only PP substrate is plasma treated. C. PP substrate with the epoxy resin droplet placed on it are simultaneously exposed to plasma.

2. Experimental methods and materials

2.1. Materials

Epoxy resin 506 supplied by Aldrich was used in the investigation. The density of epoxy resin was: 1.168 g/cm^3; the dynamic viscosity was 500–700 cps.

Extruded polypropylene (PP) films were used as substrates; the roughness of the films was established with AFM as 10–20 nm. AFM study was carried out with a Park 5 M scanning probe microscope (Scientific Park Instruments). PP film samples, with dimensions of 25×25 mm and a thickness h of 25 ± 1 μm (as established with the digital micrometer), were thoroughly cleaned with ethanol and acetone and dried under ambient conditions.

2.2. Methods

For elucidation of the influence of cold plasma on the surface properties of liquid epoxy resin three series of experiments marked A, B and C were carried out.

Series A. Non-treated 5 μl epoxy droplets were placed on the non-treated PP substrates and the apparent (or "as placed", see Ref. [34]) contact angles were taken (see Fig. 1A). The droplets were placed with the precise micro-syringe Thermo Scientific Finnpipette F1.

Series B. Non-treated 5 μl epoxy droplets were placed on the plasma-treated PP substrates and the apparent contact angles were taken (see Fig. 1B). The experimental data related to the series B are denoted by the subscript 1 in the text.

Series C. The 5 μl epoxy droplets were placed on the PP substrates and altogether introduced in the cold plasma chamber. Thus, both the epoxy resin droplet and the PP substrate were exposed to the plasma treatment, as shown in Fig. 1C. After the plasma treatment the apparent contact angles were established. The experimental data related to the series C are denoted by the subscript 2 in the text.

The experiments in all series were repeated 10 times for the CA, and 5 times for the CAH measurements. The results were averaged. The contact angles were measured immediately after and also within 24 and 48 h after the plasma treatment.

The parameters of the radiofrequency plasma discharge were: the plasma frequency was 13.56 MHz; the power was 18 W; the pressure was 2 Torr; the times of irradiation were varied: 10, 20 and 30 s; the volume of the discharge chamber was 840 cm^3.

Dried compressed air was supplied by Oxygen & Argon Works, Ltd., Israel; moisture was less than 10 ppm, the concentration of oxygen was 20–22%. The nitrogen was supplied by Oxygen & Argon Works, Ltd., Israel; moisture and oxygen was less than 2 ppm, carbon dioxide was less than 1 ppm, the concentration of nitrogen was 99.999%.

Apparent contact angles were established using the Ramé–Hart goniometer (Model 500). Eight measurements were taken to calculate mean apparent contact angles at ambient conditions. The apparent contact angles were taken on both sides of a droplet; the results were averaged.

Contact angle hysteresis was established with the tilted plane method. A 5 μl epoxy resin droplet was placed on PP film mounted on the glass slide. The slide was tilted until the drop began to move. The front and rear contact angles at which the droplet started to slip are regarded as the advancing θ_{adv} and receding θ_{rec} contact angles, correspondingly, as depicted in Fig. 2. The difference $\Delta\theta = \theta_{adv} - \theta_{rec}$ is called the contact angle hysteresis [35–37]. In spite of the fact that the "tilted plane experiment" was criticized as a method for the accurate establishment of the contact angle hysteresis, it is still broadly used for its estimation [39]. It should be stressed that for the epoxy resins, possessing relatively high viscosity and zero evaporation rate, the tilted plane method is the only applicable