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Towards understanding hydrophobic recovery of plasma treated polymers: Storing in high polarity liquids suppresses hydrophobic recovery

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ABSTRACT

The phenomenon of hydrophobic recovery was studied for cold air plasma treated polyethylene films. Plasma-treated polymer films were immersed into liquids with very different polarities such as ethanol, acetone, carbon tetrachloride, benzene and carbon disulphide. Hydrophobic recovery was studied by measurement of contact angles. Immersion into high polarity liquids slows markedly the hydrophobic recovery. We relate this slowing to dipole–dipole interaction of polar groups of the polymer with those of the liquids. This kind of interaction becomes decisive when polar groups of polymer chains are at least partially spatially fixed.

1. Introduction

Plasma treatment is broadly used for modification of surface properties of polymer materials [1,2]. The plasma treatment creates a complex mixture of surface functionalities which influence surface physical and chemical properties and results in a dramatic change in the wetting behaviour of the surface [3–11]. Not only the chemical structure but also the roughness of the surface is affected by the plasma treatment, which also could change the wettability of the surface [12]. Plasma treatment usually strengthens hydrophilicity of treated polymer surfaces. However, the surface hydrophilicity created by plasma treatment is often lost over time. This effect of decreasing hydrophobicity is called "hydrophobic recovery" [13–21]. The phenomenon of hydrophobic recovery is usually attributed to a variety of physical and chemical processes, including: (1) re-arrangement of chemical groups of the surface exposed to plasma treatment, due to the conformational mobility of polymer chains; (2) oxidation and degradation reactions at the plasma treated surfaces; (3) diffusion of low molecular weight products from the outer layers into the bulk of the polymer, (4) plasma-treatment induced diffusion of additives introduced into the polymer from its bulk towards its surface [19]. Occhiello et al. classified the complicated processes occurring under hydrophobic recovery according their spatial range, i.e. short-range motions within the plasma-modified layer, burying polar groups away from the surface and long-range motions, including diffusion of non-modified macromolecules or segments from the bulk to the surface [22]. A phenomenological model of hydrophobic recovery has been proposed recently by Mortazavi and Nosonovsky [20].

At the same time, the precise mechanism of this effect remains obscure. We demonstrate in our paper that dipole–dipole interaction of the plasma treated polymer and molecules of the surrounding medium plays an important role in the hydrophobic recovery.

2. Experimental

Extruded low-density polyethylene (LDPE) films were exposed to cold air radio frequency inductive plasma under following conditions: frequency about 10 MHz, power 100 W, pressure 6.7×10^{-2} Pa. The time span of irradiation was 1 min. Immediately after the treatment films were immersed in organic liquids: ethanol (dehydrated), C_2H_5OH, acetone, $(CH_3)_2CO$ and carbon tetrachloride, CCL_4 all supplied by Bio-Lab Ltd., Israel, benzene, C_6H_6 by

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Table 1
Parameters of hydrophobic recovery (fitted according to Exp. (1)), observed with various liquids.

Liquid	Molecular dipole moment, D	τ, days $t = 30\,^{\circ}$C	τ, days $t = 8\,^{\circ}$C	θ_{sat},° $t = 30\,^{\circ}$C	θ_{sat},° $t = 8\,^{\circ}$C
Acetone	2.88	0.046	1.25	55	54.6
Water	1.854	0.854	4	56.3	80
Ethanol	1.69	1.492	1.639	70.5	70
Benzene	0	0.013	0.649	79	96
CS_2	0	0.001	0.026	90.7	107
CCl_4	0	0.01	0.578	82	89

Fluka Chemika and Carbon disulphide, CS_2 by Riedel-de-Haen. The roughness of LDPE films was established as 50 ± 4 nm measured by AFM (Park 5 M scanning probe microscope, Park Scientific Instruments, CA, USA). The roughness of the LDPE film did not change after plasma treatment. Two series of experiments were carried out at the different temperatures of liquids: the first under the temperature of $30 \pm 3^{\circ}$, and the second under the temperature of $8 \pm 2^{\circ}$.

In addition, the hydrophobic recovery of LDPE films was studied at ambient conditions (temperature $25 \pm 5^{\circ}$) and air humidity 30–40%, and also when the irradiated films were kept under low vacuum.

Contact angles (static and advancing) were measured by a Ramé-Hart Advanced Goniometer Model 500-F1. The advancing contact angle was measured by the needle-syringe method. For the study of the hydrophobic recovery the contact angles (static and advancing) were measured every 2 h during the first 12 h after the plasma treatment; thereafter contact angles were taken every 24 h. Before measurement of contact angles, the LDPE films were dried for 10 min at the low vacuum of 6.7×10^{-2} Pa at the ambient temperature. Measurements were made on both sides of the drop and were averaged. A series of 5 experiments was carried out for every aforementioned immersion liquid.

3. Results and discussion

Graphs presenting the hydrophobic recovery of LDPE films immersed at different temperatures in various organic liquids are depicted in Figs. 1–2. Graphs presenting hydrophobic recovery of the same films kept in humid air and vacuum are presented in Fig. 3. The time dependencies of the static contact angle were approximated by the empirical formula:

$$\theta(t) = \tilde{\theta}(1 - e^{-t/\tau}) + \theta_0 = \theta_{sat} - \tilde{\theta}e^{-t/\tau} \quad (1)$$

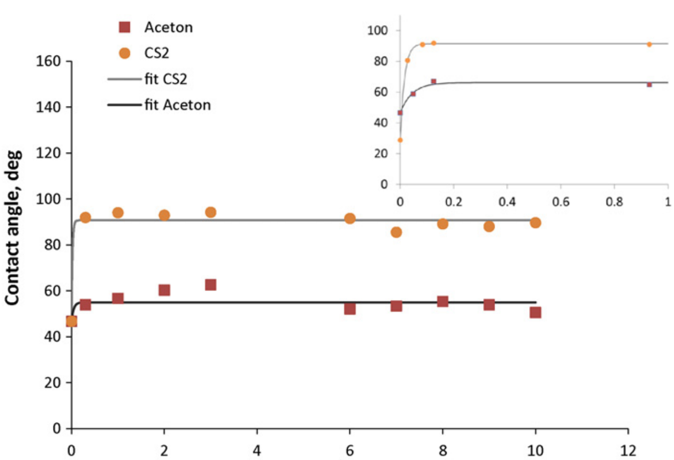

Fig. 1. Hydrophobic recovery of LDPE films immersed at 30° in various organic liquids. Inset depicts the effect during the first day of recovery. Solid lines represent the exponential fitting with Exp. (1).

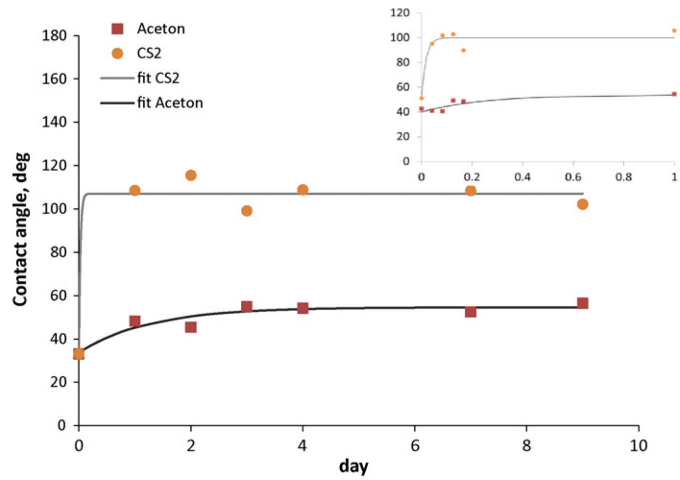

Fig. 2. Hydrophobic recovery of LDPE films immersed at 8° in various organic liquids. Inset depicts the effect during the first day of recovery. Solid lines represent the exponential fitting with Exp. (1).

where θ_0 corresponds to the initial contact angle established immediately after the plasma treatment, τ is the characteristic time of restoring of the contact angle, $\tilde{\theta}$ is the fitting parameter, and $\theta_{sat} = \tilde{\theta} + \theta_0$ corresponds to the saturation contact angle. Parameters τ and θ_{sat} established by the fitting of the experimental data according to Eq. (1) for various immersion liquids are summarized in Table 1. It is noteworthy that the same exponential fitting satisfactorily describes the process of hydrophobic recovery at both the initial and advanced stages of the films' ageing. The most important physical parameter established by this fitting for immersed films is the characteristic time of restoring of the contact angle τ, and at the first glance it should be compared to that established for plasma treated LDPE films stored in vacuum and in humid air

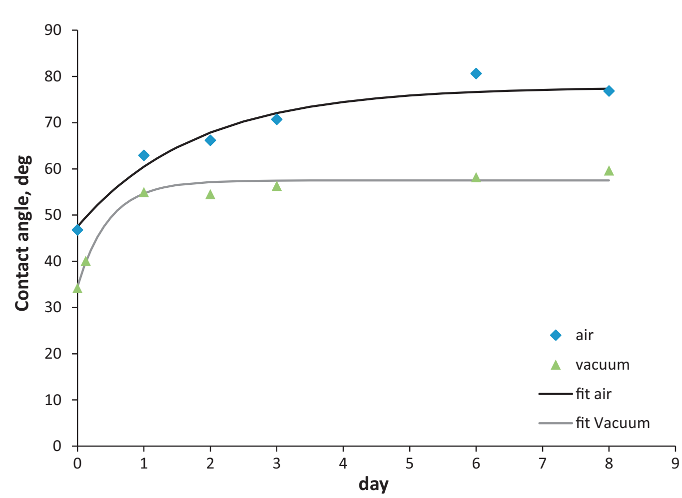

Fig. 3. Hydrophobic recovery of LDPE films in humidity of the air 30–40% and in vacuum. Solid lines represent the exponential fitting with Exp. (1).