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Physical mechanisms of interaction of cold plasma with polymer surfaces

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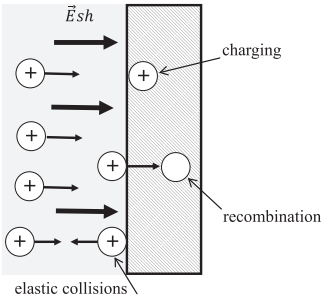
GRAPHICAL ABSTRACT



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ABSTRACT

Physical mechanisms of the interaction of cold plasmas with organic surfaces are discussed. Trapping of plasma ions by the CH_2 groups of polymer surfaces resulting in their electrical charging is treated. Polyethylene surfaces were exposed to the cold radiofrequency air plasma for different intervals of time. The change in the wettability of these surfaces was registered. The experimentally established characteristic time scales of the interaction of cold plasma with polymer surfaces are inversely proportional to the concentration of ions. The phenomenological kinetic model of the electrical charging of polymer surfaces by plasmas is introduced and analyzed.

1. Introduction

Plasma treatment (low and atmospheric-pressure) is broadly used for modification of the surface properties of polymer materials [1–6]. The plasma treatment creates a complex mixture of surface functionalities which influence physical and chemical properties of polymers, and results in a dramatic change in the wetting behavior of the surface; this is true for both solid and liquid surfaces [7–17]. 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 [18]. Plasma treatment usually strengthens the hydrophilicity of treated polymer surfaces. However, the surface hydrophilicity created by plasma treatment is often lost over time. This effect of decreasing hydrophilicity is called "hydrophobic recovery" [19–28]. The phenomenon of hydrophobic recovery is usually attributed to a variety of physical and chemical processes; however, their influence remains highly debatable [19–28].

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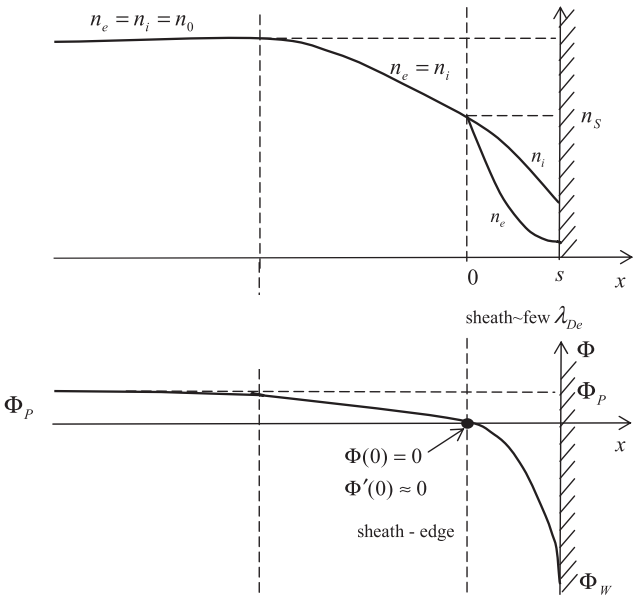

Fig. 1. Scheme of a sheath in a contact with the wall for the DC plasma; n_e; n_i are the concentrations of electrons and ions respectively, Φ is the potential; Φ_P, Φ_W are the potentials of the plasma and wall respectively; λ_{De} is the Debye length.

Our investigation is focused on the interaction of so-called "cold" plasma discharges with organic-polymer surfaces which are generally solid or liquid. The "cold" plasma discharges are characterized by the temperatures of electrons $T_e \cong 1$–10 V and temperatures of ions which are much lower, than those of electrons $T_i \ll T_e$ (recall that the temperature associated with $T = 1$ V equals 11605 K). The concentration of charge carriers in cold plasmas is typically $n \approx 10^{14}$–10^{19} m^{-3} (see Ref. [29]).

Plasmas are joined to solid surfaces across thin positively charged layers called sheaths [29], depicted in Fig. 1. The origin of plasma sheaths may be understood on account that the electron thermal velocity is much larger than the ion thermal velocity. Thus, at the surface bounding cold plasma, a potential exists to contain the more mobile charged species [29]. This allows the flow of positive and negative carriers to the wall to be balanced. In the usual situation of the plasma, consisting of equal numbers of positive ions and electrons, the electrons are far more mobile than the ions. The plasma will therefore be charged positively with the respect to a grounded wall. Plasma sheaths accelerate ions and it is reasonable to attribute the modification of organic surfaces by plasmas to the collisions of ions accelerated by the electric field of a sheath with the moieties constituting an organic surface. The electrons of the sheath practically do not transfer energy to much heavier organic moieties forming the surface [29]. The typical thickness of plasma sheath is on the order of magnitude of the Debye length [29]. In spite of the great theoretical and experimental effort spent on the investigation of the interaction of cold plasmas with organic surfaces, the mechanism of this interaction remains obscure. Our study introduces these mechanisms as verified by the experimental research, thus validating the theoretical assumptions.

2. Experimental

Smooth polymeric samples were prepared with low density polyethylene LDPE (Carmel Chemicals Ltd.) by hot pressing with atomically flat heated plates. LDPE films with a thickness of 1 mm manufactured by extrusion were sandwiched between aluminum foil and a steel computer hard disk with a diameter of 10 cm, which was atomically flat. Then the sandwich was pressed under pressure of 1.3 MPa and a temperature of 170 °C for 30 min. The sample was cooled at ambient conditions. The roughness of the pressed LDPE films was established with AFM as 5–10 nm. The thickness of the LDPE films was 0.7 ± 0.1 mm.

The LDPE films were exposed to a radiofrequency (13 MHz) inductive air plasma discharge under the following parameters: pressure $P = 0.5$, 1.0 and 2.0 Torr, power 18 W under an ambient temperature. The details of the experimental setup are supplied in Ref. [26]. For every pressure value, series of measurement of the contact angle, which is supposed to be connected to the surface charge density, was carried out for several exposition times: 0.05, 0.10, 0.15, 0.30, 0.50, 0.70, 1.00, and 3.00 s.

Contact angles were measured with the Ramé-Hart Advanced Goniometer Model 500-F1. A series of 10 experiments was carried out for every sample. The results were averaged.

3. Results and discussion

3.1. Experimental study of the interaction of cold plasma with polymer surfaces

It is well-known that plasma treatment strongly modifies (increases) the surface energy of polymer materials [1–4]. The natural macroscopic measure of the surface energy is the apparent contact angle [30,31]. The accurate experimental establishment of the contact angle turns out to be a challenging task, due to the phenomenon of the contact angle hysteresis [32–37]. However, for atomically smooth polymer surfaces, the effect of the contact angle hysteresis is not essential and may be neglected. Hence, for the characterization of plasma irradiated LDPE surfaces we used the so called "as placed" apparent contact angle (APCA), introduced recently by Tadmor et al. [37]. Thus, the measurement of the "as placed" APCA on plasma treated LDPE films (according the procedure described in Section 2) supplies at least qualitative information about the processes occurring on the polymer surfaces, exposed to plasma. The kinetics of the change of APCA with the time of exposure is depicted in Fig. 2.

Time dependence of the contact angle on time t was fitted by the following empiric expression:

$$\theta(t) = \tilde{\theta} \exp\left(-\frac{t}{\tau_{\exp}}\right) + \theta_{sat}, \quad (1)$$

where θ is the APCA, θ_{sat} is the empiric saturation contact angle corresponding to the infinite time of plasma irradiation, $\tilde{\theta} + \theta_{sat}$ is the initial APCA, and $\tau_{\exp}$ is the experimentally established characteris-

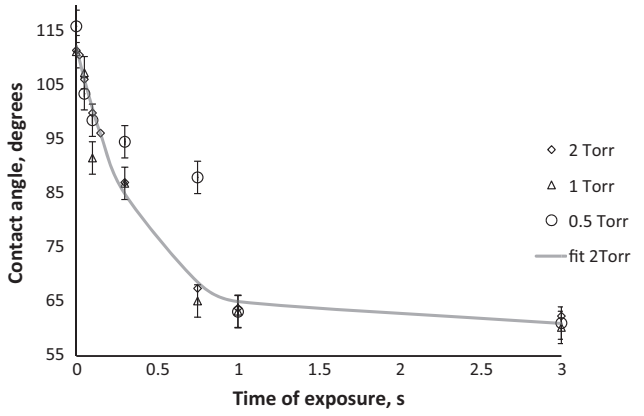

Fig. 2. The kinetics of the change of apparent contact angle with the time of exposure of LDPE film to plasma. The solid line represents the exponential fitting of experimental data for the pressure of 2 Torr.