

Activation of polyethylene and polypropylene in atmospheric pressure glow discharge

M. ŠÍRA, P. ŠTAHEL, V. BURŠÍKOVÁ, J. VOHÁNKA, D. TRUNEC

*Department of Physical Electronics, Faculty of Science, Masaryk University,
Kotlářská 2, 611 37 Brno, Czech Republic*

Received 23 April 2004

The atmospheric pressure glow discharge was used for activation of polymer materials. The discharge was generated between two plane metal electrodes covered by a glass dielectric barrier. The discharge was ignited in pure nitrogen or in mixtures of nitrogen with hydrogen or nitrogen with ammonia. Studied polymers were polyethylene and polypropylene. The surface energy of both activated and non-activated polymers was determined by means of contact angle measurements. The influence of treatment time on the surface free energy of polymers was studied.

PACS: 52.77.Bn, 52.80.Hc

Key words: plasma activation, atmospheric pressure glow discharge, surface free energy, polymers

1 Introduction

The dielectric barrier discharge (DBD) is one of the widely used low-temperature non-equilibrium plasma sources at the high pressure. It is used for industrial purposes such as ozone generation, modification of polymers, depollution, surface treatment and thin film deposition. This discharge is usually filamentary at the atmospheric pressure [1]. This causes a lack of homogeneity and leads to the non-uniform treatment. At certain conditions it is possible to obtain homogenous barrier discharge – so called atmospheric pressure glow discharge (APGD) [2], which is very interesting for applications related to the surface treatment.

Polymers are very often used as films and foils for packaging, protective coatings, sealing applications etc. Their low surface energy may be desirable for several applications, but for other applications it is a disadvantage, which has to be overcome. Thus the surface pretreatment is required to achieve satisfactory adhesion for printing, painting, metalisation etc. [3, 4]. The plasma modification is one of possible methods to enhance the surface free energy with many advantages.

In this study polyethylene and polypropylene have been activated in the atmospheric pressure glow and changes of the surface free energy were studied.

2 Experimental

2.1 Experimental setup

The dielectric barrier cell consisted of two parallel plane electrodes. The upper one was covered by glass dielectric (simax glass, 2 mm thick), the lower one was covered by dielectric made of polymer samples, e.g. commercially available high density polyethylene (PE) or polypropylene (PP) plate of thickness 1 mm and surface area approximately

8 cm × 12 cm. Before plasma treatment the polymer samples were cleaned in a mixture of cyclohexane and isopropylalcohol with ratio 1:1. The discharge gap was 1 mm thick. The upper electrode was periodically moving over the substrate in order to ensure even greater homogeneity of plasma activation. The high voltage was connected to the upper electrode and the operating frequency was 10 kHz. The input power was set 25 W. Time of application of the discharge varied from 11 seconds to 5 minutes.

Before the start of the experiment the discharge cell was pumped down to 1 kPa and then filled by the gas to the pressure of 101 kPa. Used gases were nitrogen (flow rate 3 slpm), mixture of nitrogen and hydrogen of flow rate ratio 0.03 and nitrogen with ammonia of flow rate ratio 0.0037. The atmospheric pressure was maintained by slight pumping during the discharge. The input power and the composition of mixtures were chosen to maintain stable glow discharge.

2.2 Surface free energy

Contact angles between testing liquids and polymers were measured to determine the total surface free energy using a sessile drop technique [6]. Liquid drops on the plasma – activated polymer surface were imaged by CCD camera and the contact angle was measured. 6 liquids were used: distilled water, 1, 2 – ethanediol, diiodomethane, formamide, 1, 2, 3 – propanetriol (glycerol) and 1–bromo–naphthalene. Contact angles were measured at the least at 10 drops (each 2 μl) for every liquid. So called “multiple regression acid–base” theory [5] was used to calculate the total surface free energy and its components expressed by the equation:

$$\gamma = \gamma^{LW} + \gamma^{AB},$$

where γ^{LW} means the total apolar (dispersive) Lifshitz–van der Walls interaction and γ^{AB} acid–base or electron–acceptor/electron–donor interaction according to Lewis [6]:

$$\gamma^{AB} = 2\sqrt{\gamma^+\gamma^-},$$

where γ^+ is the electron–donor component and γ^- the electron–acceptor component. The surface free energy is calculated from the Young–Dupré’s equation using the contact angle θ :

$$(1 + \cos \theta_i) \gamma_i = 2 \left(\sqrt{\gamma_i^{LW} \gamma_j^{LW}} + \sqrt{\gamma_i^+ \gamma_j^-} + \sqrt{\gamma_i^- \gamma_j^+} \right).$$

The subscript i refers to the testing liquid and j to the studied material.

3 Results

The surface free energy of untreated polyethylene was (39 ± 2) mJ/m² and of untreated polypropylene (34 ± 3) mJ/m². Dependence of the surface free energy on the treatment time was determined for both PE and PP polymers.

In the first case, the working atmosphere was nitrogen at flow rate 3 slpm. The surface free energy of PE treated in the nitrogen plasma with the input power 25 W is shown

in Fig. 1. The highest value of the surface free energy was 54 mJ/m^2 after 7 seconds of treatment. The values did not change significantly for mixtures of nitrogen with hydrogen and nitrogen with ammonia. The only difference was that the highest value of the surface free energy was achieved after 20 s of treatment in both cases. The lowest value of contact angle of the substrate with distilled water was 32° , see Fig. 2.

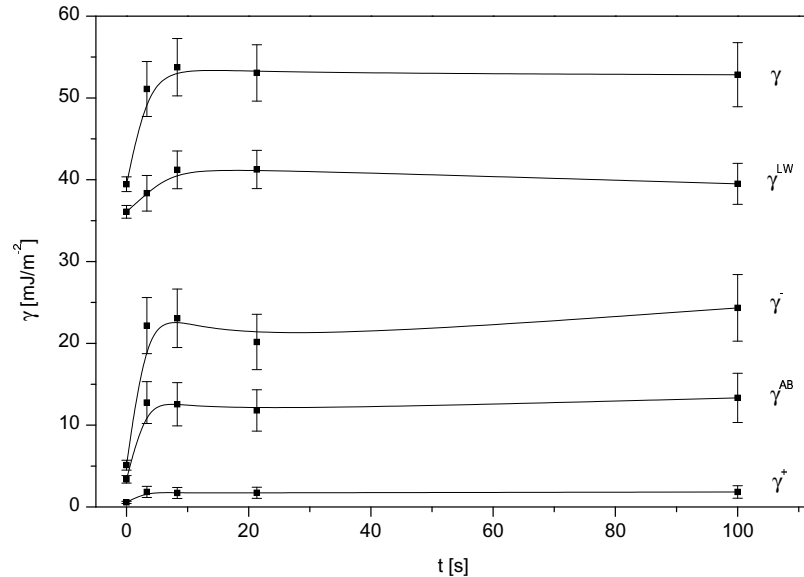


Fig. 1. Dependence of the surface free energy of polyethylene on the treatment time in nitrogen for input power 25 W determined by means of acid–base theory. γ – surface free energy, γ^{LW} – dispersion part, γ^{ab} – polar part, γ^+ – acid part, γ^- – base part.

The surface free energy of PP treated in nitrogen plasma with the input power 25 W is shown in Fig. 3. The highest value of the surface free energy was 53 mJ/m^2 after 7 s of treatment. Again for other mixtures of gasses the highest surface free energy did not change significantly, but it was achieved after 20 s of treatment. The lowest contact angle of distilled water was 42° .

4 Conclusions

A large set of plasma activated polypropylene and polyethylene samples was prepared in atmospheric pressure glow discharge in order to find the optimum treatment conditions. Analysis of the activated surfaces was done using contact angle measurements. The surface homogeneity of activated samples was ensured by the use of atmospheric pressure glow discharge and moveable upper electrode.

The surface free energy of polyethylene obtained in optimum conditions was 54 mJ/m^2 and the contact angle of water 32° . Similar treatment of high density polyethylene in the filament atmospheric pressure discharge was described in [4], where achieved water contact angle of 54° was reported.

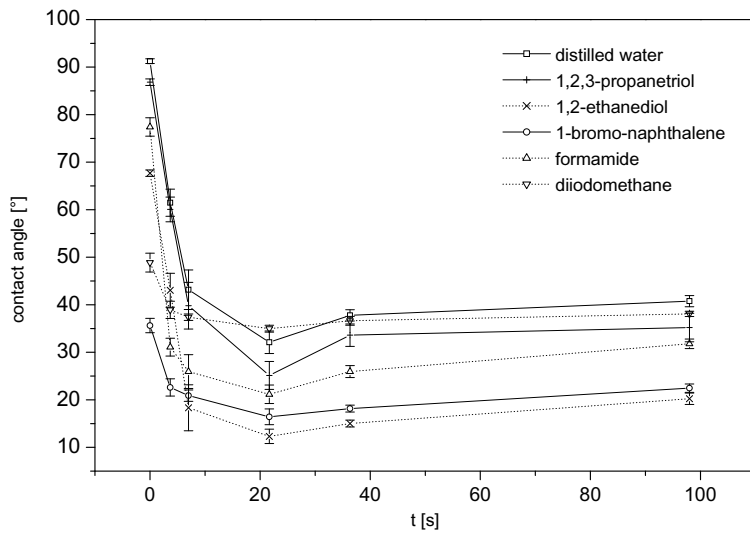


Fig. 2. Dependence of the contact angle of various liquids with polyethylene on the treatment time in nitrogen–ammonia plasma for input power 25 W.

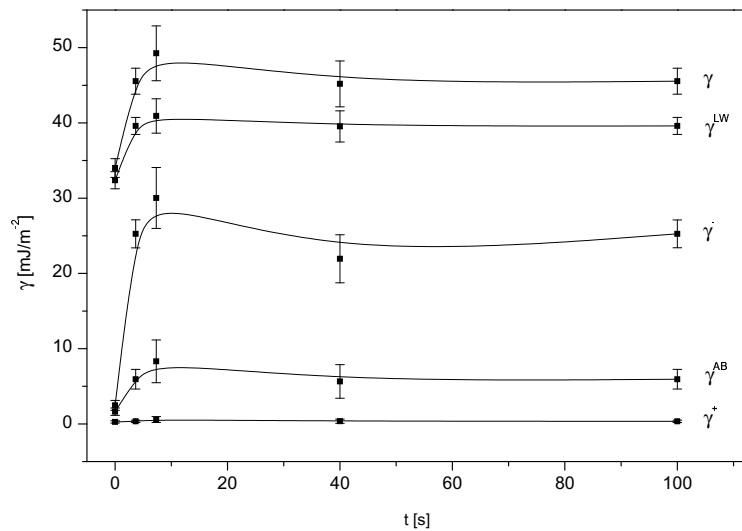


Fig. 3. Dependence of surface free energy of polypropylene on the treatment time in the nitrogen for input power 25 W determined by means of acid–base theory. γ – surface free energy, γ^{LW} – dispersion part, γ^{AB} – polar part, γ^+ – acid part, γ^- – base part.

The surface free energy of polypropylene obtained in optimum conditions was 53 mJ/m² and the contact angle of water 42°. Similar treatment of PP in the filament atmospheric pressure discharge was described in [3], where achieved water contact angle of 49° was reported.

From our experiments we can conclude that APGD is more suitable for polymer surface treatment. This is also supported by AFM and SEM measurements of samples treated in filamentary and glow discharge.

This research has been supported by grants 202/02/0880 and 202/02/D097 of Grant Agency of the Czech Republic.

References

- [1] R. Brandenburg, K. V. Kozlov, F. Massines, P. Michael, H. Wagner: Proceedings of HAKONE VII, Greifswald (2000).
- [2] D. Trunec, A. Brablec, J. Buchta: *J. Phys. D: Appl. Phys.* **34** (2001) 1697.
- [3] D.J. Upadhyay, Nai-Yi Cui, C.A. Anderson, N.M.D. Brown: *Surface oxygenation of polypropylene using an air dielectric barrier discharge: the effect of different electrode-platen combinations*; *Applied Surface Science*, in press.
- [4] G. Borcia, C.A. Anderson, N.M.D. Brown: *The surface oxidation of selected polymers using an atmospheric pressure air dielectric barrier discharge*; *Applied Surface Science* **221** (2004) 203.
- [5] Z. Navrátil, V. Buršíková, P. Stahel, M. Šíra, P. Zvěřina: *On the Analysis of Surface Free Energy of DLC Coatings Deposited in Low Pressure RF Discharge*; in proceedings of this conference.
- [6] R. J. Good: *Contact Angle, Wettability and Adhesion*; ed. K. L. Mittal. VSP BV, Utrecht (1993).