Bulgarian Journal of Physics 19, Nos 1/2 (1992) 89–94

SURFACE MODULATION OF POLYIMIDE IN A GAS DISCHARGE: POST-EFFECT

S. I. Ivanov, D. M. Svirachev, V. P. Pechenyakova,
Sofia University, Faculty of Physics,
5, J. Bouchier Blvd., 1126 Sofia, Bulgaria

Ch. V Petrov, E. D. Dobreva
Technical University, Department of Chemistry,
1156 Sofia, Bulgaria

Received 26 July 1991

Abstract. The evolution of a polyimide surface treated in a corona discharge for 0.3 s have been investigated. The relaxation was followed from the 12th minute up until 500 hours after discontinuation of the plasma treatment. The acquired adhesivity of the treated surface gradually decreases during ageing, and this is expressed by decrease of the cosine of the wetting angle. The decrease with time of the adhesivity acquired from the treatment follows a law expressed as the sum of two exponents. This is explained in terms of deactivation of two types of adhesive states generated from the action of the corona discharge. The first adhesive state has a lifetime of 17 hours and relative content 0.16. The second adhesive state lasts longer — it has a lifetime of 3140 hours and relative content 0.81.

Резюме. Исследована эволюция полиимидной поверхности, которая была обработана в коронном разряде в продолжении 0,3 s. Релаксация прослеживается с 12 минуты до 500 часов после обработки. В процессе релаксации дополнительная адхезивность обработанной поверхности постепенно уменьшается, что выражается уменьшением косинуса контактного угла смачивания. Уменьшение во времени дополнительной адхезивности следует закону, которой выражается как сумма двух экспонент. Такой результат объясняется дезактивацией двух видов адхезионных состояний, генерированных действием коронного разряда. Первое адхезионное состояние имеет время жизни 17 часов и отностельное участие 0,16, а второе соотвественно 3140 часов и 0,81.

1. Introduction

According to Liston and Rose [1], the polyimide Kapton type H possesses initial surface free energy of 40 mJ.m^{-2}. This value characterizes the polyimide as a polymer of insufficient polarity, from the point of view of adhesion technology, and that is why it must be subjected to surface modification. In this case the term "surface modification" must be defined as in one of the particular meanings, namely, increase of the surface tension or improvement of the adhesivity of the polymer. The modification resulting in adhesion activation of the polymer surfaces is achieved relatively easily by using nonisothermal plasmas generated from partial [2], corona [3], radiofrequency [4,5], or microwave discharges [5]. On the whole, the interaction of the various forms of gas discharge on the polymers are analogous. More essential is the influence of the type of working gas and the exposure dose.

This article describes and discusses the results from an experimental study of the changes in the surface tension of a polyimide surface treated in a corona discharge.

2. Experiment

The object of the investigation was Kapton type H foil, 75 μm thick. Kapton H is a registered trade mark of Du Pont. Treatment in a corona discharge was carried out in air in a discharge gap formed between a blade electrode and a grounded rotary metal, which were 0.5 mm apart. The polymer sample was fixed on the cylinder together with the dielectric barrier. The corona discharge was excited by an alternating volatge with average pulse amplitude 3.5 kV and frequency 7 kHz. Under these conditions the corona discharge burned in diffusion mode without any visible signs of discrete structure, and the ionized gas may be considered to be in a plasma state. Treatment duration was determined by the peripheral velocity of the grounded cylinder, by the number of passages of the sample through the discharge and by the visible width of the discharge zone. The energy state of the relaxing polymer surface was characterized by the wetting angle from using drops of deionized water. However, the wetting angle has the quality of only an initial experimental quantity which is useful in comparing and controlling the physical state of the treated surfaces. A more suitable measure — one of physical nature — for the adhesivity of a polymer surface is the cosine of the wetting angle, for which we assume that it is in a linear relation with the surface tension.

3. Results and Discussion

The behaviour of the plasma activated polyimide surface with time is of interest both to clarify the nature of the relaxation process and from the point of view of adhesion technology. The relaxation process was examined with time by the change in the wetting angle after the discontinuation of the corona action. This change could provide information about the types of the plasma-induced adhesion states, as well as about their lifetime and relative quantities.

The results are shown in Fig. 1, in terms of time dependence of the wetting angle and its cosine on time. We divided this dependence into several regions, depending on the step of the experiment and on the energy state of the polyimide surface. Region I corresponds to the initial adhesivity of the polyimide surface

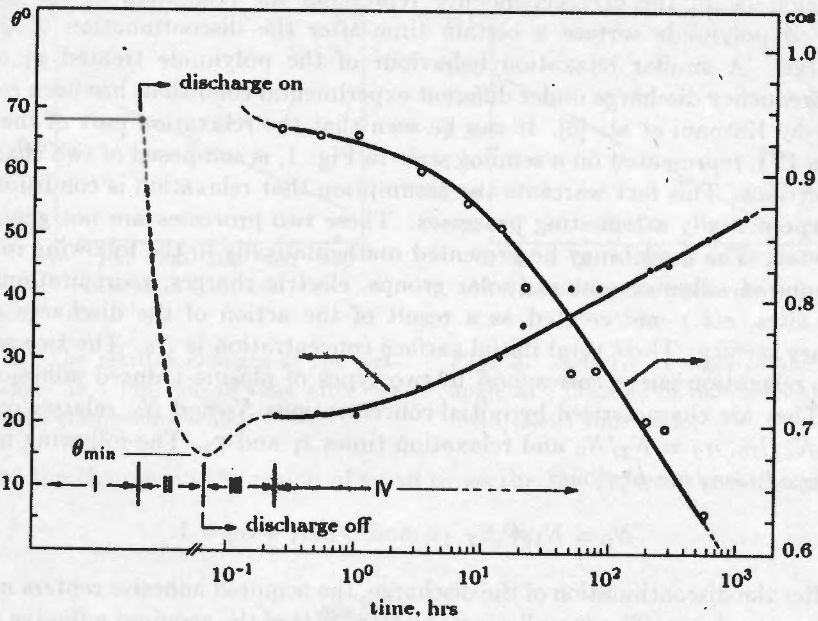


Fig. 1. The time dependence of the wetting angle at different stages of the experiment in the modification of polyimide in corona discharge. Exposure time 300 ms

before carrying out the corona activation. In our case, the state of the surface was characterized by a wetting angle of 68°. It must be pointed out that for the same quantity and for the same product Kogoma and Turban [4] found a value of 62°, while Liston and Rose [1] observed a value of 79°. The difference in the initial values of the wetting angle as found by different authors may be explained by the inevitable industrial tolerance of the polyimide type H, which is a conventional product, by the differences in the qualities of the test fluid used, and perhaps by the influence of some meteorological factors.

The second region of the $\theta(t)$ dependence corresponds to the plasma treatment step and adhesion activation. This part is represented by a dashed curve and indicates that the course of the curve is conditional. The real type of the activation part has been investigated experimentally and is linked to the respective physical model. For each set of specific physical conditions the wetting angle reaches a definite minimum value $\theta_{\min}$. However, this minimum value cannot be measured experimentally.

Region III of the dependence expresses the relaxation of the plasma-activated surface immediately after the discontinuation of the treatment. The beginning of the relaxation dependence, just as the minimum wetting angle, cannot be obtained experimentally, because of the sluggishness of the method of measuring the wetting angle. Hence the relaxation course is unknown in the millisecond and second region. However, the experiment reveals a trend towards an increase in the wetting angle, or a decrease in the acquired surface adhesivity. This loss of adhesivity is due to the deactivation of those plasma-induced adhesion centers with lifetimes of milliseconds.

Region IV of the $\theta(t)$ dependence represents the relaxation of the plasma-activated polyimide surface a certain time after the discontinuation of the gas discharge. A similar relaxation behaviour of the polyimide treated in oxygen radio-frequency discharge under different experimental conditions has been recently shown by Katnani et al. [6]. It can be seen that the relaxation part of the curve (region IV), represented on a semilog scale in Fig. 1, is composed of two characteristic sections. This fact warrants the assumption that relaxation is conditioned by two exponentially attenuating processes. These two processes are not genetically connected. The model may be presented mathematically in the following manner.

Acquired adhesive centers (polar groups, electric charges, reorientations, desorbed sites, etc.) are created as a result of the action of the discharge on the polymer surface. Their total initial surface concentration is N_0. The two sections of the relaxation curve correspond to two types of plasma-induced adhesion centers. They are characterized by initial concentrations N_1 and N_2, relative contents $\alpha_1 = N_1/N_0$, $\alpha_2 = N_2/N_0$ and relaxation times τ_1 and τ_2. The following normalizing conditions are obvious:

$$N_0 = N_1 + N_2 \qquad \text{and} \qquad \alpha_1 + \alpha_2 = 1.$$

After the discontinuation of the discharge, the acquired adhesive centers undergo spontaneous decay. The overall concentration $N(t)$ of the acquired adhesive centers decreases with time according to the following law:

$$N(t) = N_0\left[\alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2)\right]. \tag{1}$$

There are grounds to assume the existence of proportionality between the overall concentration of the adhesive centers, the corresponding surface tensions, and the cosines of the wetting angles. In such case, Eq. (1) may be presented as follows:

$$\cos\theta(t) = \cos\theta(0)\left[\alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2)\right]. \tag{2}$$

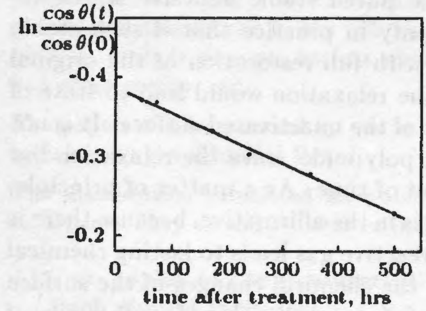
In this equation $\cos\theta(0)$ and $\cos\theta(t)$ are the values of the cosines of the initial and running wetting angles from the relaxation stage after discontinuation of the discharge.

The component with index 1 may be neglected upon surveying the process of deactivation for high values of times $t \gg \tau_1$, when the first type of adhesive centers is already deactivated. Then the following linear dependence is obtained for the relative changes in the cosine of the wetting angle:

$$\ln\frac{\cos\theta(t)}{\cos\theta(0)} = \ln\alpha_2 - \frac{t}{\tau_2}. \tag{3}$$

Let us compare the model offered above with the data from Fig. 1. To that end we compute the relative changes of the cosines of the wetting angles measured. A rectilinear dependence on time is obtained, as presented in Fig. 2. Through computation from that graph we find the following values for the relaxation time and for the relative content of the adhesive centers of the second type:

$$\tau_2 = 3140 \text{ hours} \qquad \text{and} \qquad \alpha_2 = 0.81.$$



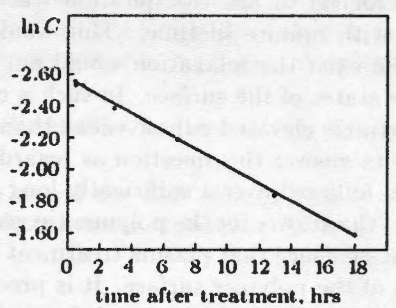


Fig. 2. The relative changes of the wetting angle as a function of time after the treatment (large time scale)

Fig. 3. Relative changes of the wetting angle as a function of time after the treatment (short time scale)

For the changes in the region of small times the Eq. (2) has the following form:

$$\ln C = \ln \alpha_1 - t/\tau_1 \tag{4}$$

where

$$C = \frac{\cos\theta(t)}{\cos\theta(0)} - \alpha_2 \exp(t/\tau_2).$$

Eq. (4) expresses a linear dependence with time. If we perform the respective computation on the basis of Eq. (4) on the experimental data from Fig. 1, we should obtain the dependence of the relative changes in the cosine of the wetting angle for the small times of the deactivation stage. This dependence is shown in Fig. 3, from which the following values are calculated for the relaxation time and for the relative content of the discharge-generated adhesive centers of the first type:

$$\tau_1 = 17 \text{ hours} \quad \text{and} \quad \alpha_1 = 0.16.$$

4. Conclusion

Two types of adhesive centers are found to be created by the gas discharge treatment. Although their lifetimes and relative contents have been determined, the absence of the requisite spectroscopic investigations does not entitle us to draw conclusions upon their nature. There are arguments in favour of the assumption that the plasma generates also other adhesive states characterized by shorter or longer lifetimes. One indication of the existence of acquired adhesive states with lifetimes shorter than those indicated in the present article is the trend toward change of the relaxation curve in its initial section. We assume that the role of plasma-induced adhesive states, with lifetimes of millisecond and second regions, is performed by the sites on the polyimide surface from which absorbed species and contaminations have been removed under the action of the gas discharge. The same is also true of the relaxation of the treated polymer in the region of the time of over 1000 hours after discontinuation of the discharge. The rising course of the relaxation curve in this region suggests unequivocally the induction of states with lifetime longer than the time limit appropriate for such an experiment.

It is logical to ask the question whether acquired stable adhesive states are created with infinite lifetime. This would signify in practice that if such stable states did exist the relaxation would not end with full restoration of the original adhesive states of the surface. In such a case the relaxation would lead to state of some lastingly elevated adhesiveness, than that of the unactivated surface. It is not possible to answer this question as regards the polyimide, since the relaxation has not been followed over a sufficiently long period of time. As a matter of principle, however, the answer for the polymers in general is in the affirmative, because there is sufficient evidence that plasma treatment in a reactive gas leads to lasting chemical changes of the polymer surface. It is precisely the chemical changes of the surface that could account for a continual rise in the surface tension and in the adhesivity of the treated polymer surface. For instance, our earlier studies indicated that plasma-treated polyethyleneterephthalate relaxes from a minimal wetting angle of 22° to a value of 37° which undergoes no further change after 500 hours. The difference between that value and the value of the natural wetting angle 68° corresponds to the lasting component of the additional adhesivity acquired from the plasma activation. A permanent component of the acquired adhesivity upon plasma treatment has been established upon polyethylene activation as well [7].

References

1 E.W. Liston and P.W. Rose. in: *Proc. 7-th Int. Symp. om Plasma Chemistry* vol. 1 (Eindhoven, 1985) 219.

2 S.I. Ivanov, D.M. Svirachev, V.P. Pechenyakova, Ch.V. Petrov and E.D. Dobreva. in: *Proc. 8-th Int. Symp. on Plasma Chemistry* vol. 4 (Tokyo, 1987) 1827.

3 S.I. Ivanov, V.P. Pechenyakova, D.M. Svirachev,, Ch.V. Petrov and E.D. Dobreva. in: *Proc. XIX-th Int. Conf. on Phenomena in Ionized gases* vol. 3 (Belgrad, 1989) 526.

4 M. Kogoma and G. Turban. *Plasma Chem. Plasma Process.* 6 (1986) 349.

5 A.M. Wrobel, B. Lamontagne and M.R. Wertheimer. *Plasma Chem. Plasma Process.* 8 (1988) 315.

6 A.D. Katnani, A. Knoll and M.A. Mycek. *J. Adhesion Sci. Technol.* 3 (1989) 441.

7 M. Pavlova, N. Novakov, M. Draganova and St. Ivanov. *Adhesion* 9 (1981) 329.