The Influence of the Surface Cross-linking of the High-Density Polyethylene Induced by Plasma Treatment on the Durability of Treatment Efficiency

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SYNOPSIS

The structure of the surface cross-linking layer of high-density polyethylene (HDPE) produced by plasma treatment was studied by DSC, X-ray diffraction, elemental analysis, and infrared analysis. The relationship between the cross-linking and the durability of the modification efficiency provided by the plasma treatment was investigated. The results of the structure analysis indicated that the polar groups introduced by the plasma just locate on the upper surface of the cross-linking layer and the chemical constitution and structure of the inner part of the cross-linking layer is similar to that of the uncross-linking HDPE. The cross-linking density of the gel decreases from the surface to the inside with a large gradient and the average cross-linking degree of the whole gel is rather low. Nevertheless, the experiment proved that this cross-linking layer can limit the mobility of the molecules in the cross-linking layer and hinder the decay of the treatment efficiency significantly. When the surface cross-linking induced by plasma reaches a certain extent, the treatment efficiency will remain relatively constant in storage. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In the last two decades, plasma polymer interactions have been actively studied because of their unique ability to surface modify polymers without affecting their bulk properties.[1,2] A great deal of improvement of the surface properties, such as wettability, dyeability, adhesivity, and the resistivity to environment attack, can be obtained by the plasma treatment. Nevertheless, it is well known that the surface modification efficiency introduced by the plasma treatment decays with time, and in many cases, after a certain length of time, the improvement provided by the treatment is almost completely lost. In 1981, Yasuda et al. reported their study on the decay of wettability of polymers of different cross-linking degree and concluded that the burying of polar groups by the plasma treatment into the bulk phase of the polymer plays a major role in the decay phenomenon and that the cross-linking of the molecules can hinder this process.[3] As we know, in many polymers, the plasma treatment will simultaneously induce the surface cross-linking of the polymers.[4-7] However, how this surface cross-linking layer affects the decay process has rarely been reported in the literature.

We previously reported the incorporation of the radicals and polar groups into the HDPE as well as the surface etching and surface cross-linking on HDPE by the plasma treatment and discussed their effects on the surface properties of HDPE.[7-10] In this study, we focus our emphasis on the investigation of the structure and properties of the surface cross-linking induced by the plasma and the effect of this cross-linking layer on the decay process of the surface energy of HDPE.

EXPERIMENTAL

Sample Preparation

The HDPE sample sheets (0.3 mm thick) were made from commercial-grade HDPE resin (MI = 3.3),

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trimmed into desired sizes, and washed consectively with acetone and petroleum ether before use. The gases used in this experiment were pure argon, hydrogen (> 99.99%), and industrial oxygen (> 99%) and were used as received.

Plasma Treatment System and Treatment Procedure

The plasma treatment was carried out in the equipment shown schematically in Figure 1. The reaction chamber is made of glass and is fitted with a gas inlet, pressure gauge, and vacuum system and is capacitively coupled by an rf power generator that operates at a fixed frequency of 13.56 MHz. The treatment pressure is controlled by the flow rate of the treatment gas that is inleted through a very fine metering valve. The samples were hung in a glass slide and mounted inside the reaction tube between two capacitive couple rings.

The plasma treatment was carried out as follows: First, the treatment system was evacuated by a rotary pump through a cold trap with liquid nitrogen to a base pressure of about 5×10^{-3} Torr, and then the treatment gas was introduced into the system to carry out the purge cycles three times. Finally, the predetermined pressure was established and the rf power was switched on.

Characterization

The analyses of the treated samples were carried out in two ways: One is directly performed on the surface of the treated samples, and the other is performed on the cross-linking fraction (gel) that was obtained from the samples by extracting and separating the soluble fraction in the totuene by a Soxhlet extractor.

The elementary analysis of the gel was carried out in Hereaus CHN-0-Rapid elementary analyzer. X-ray diffraction was obtained in the Turm-62 X-ray diffractometer. The thermal behavior of the gel was measured by a Perkin-Elmer 2C differential scanning calorimeter (N_2 protection, 10°C/min, prescanning the samples to eliminate the effect of the thermal history). The infrared analysis was performed in an Analect RFX-65 FT-IR spectrometer. The contact angles of the water and diiodomethane on the sample were measured at 25°C using an Erma contact angle meter G-1 with a goniometer. For durability measurement, the samples were stored in container with silica-gel desiccant.

The surface energies of the samples were calculated from the following formula proposed by Wu[11]:

$$(1 + \cos \theta_1) r_1 = 4 \left(\frac{r_1^d \cdot r_s^d}{r_1^d + r_s^d} + \frac{r_1^p \cdot r_s^p}{r_1^p + r_s^p} \right) \quad (1)$$

$$(1 + \cos \theta_2) r_2 = 4 \left(\frac{r_2^d \cdot r_s^d}{r_2^d + r_s^d} + \frac{r_2^p \cdot r_s^p}{r_2^p + r_s^p} \right) \quad (2)$$

where r is the surface energy; footnotes 1, 2, and s represent water, CH_2I_2, and HDPE, respectively and supercripts d and p represent the dispersion force and the polar force of the surface energy, respectively.

RESULTS AND DISCUSSION

The Structure of the Cross-linking Layer

It has been demonstrated in a previous paper that the surface cross-linking of the HDPE occurs as soon

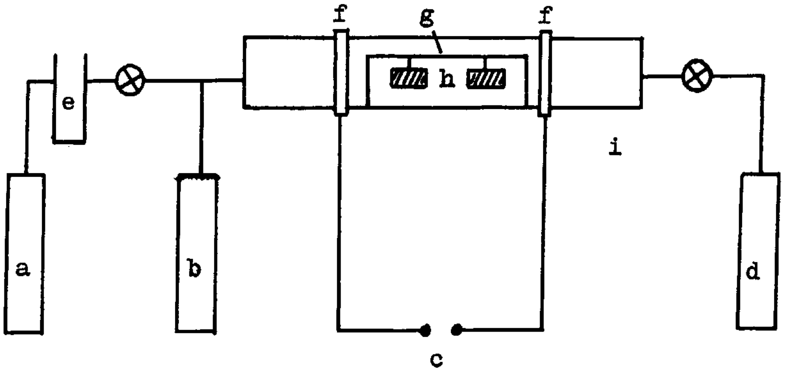

Figure 1 Plasma treatment system: (a) vacuum pump; (b) pressure gauge; (c) radiofrequency source; (d) treatment gas; (e) cold trap; (f) electrodes; (g) sample slide; (h) samples; (i) chamber.

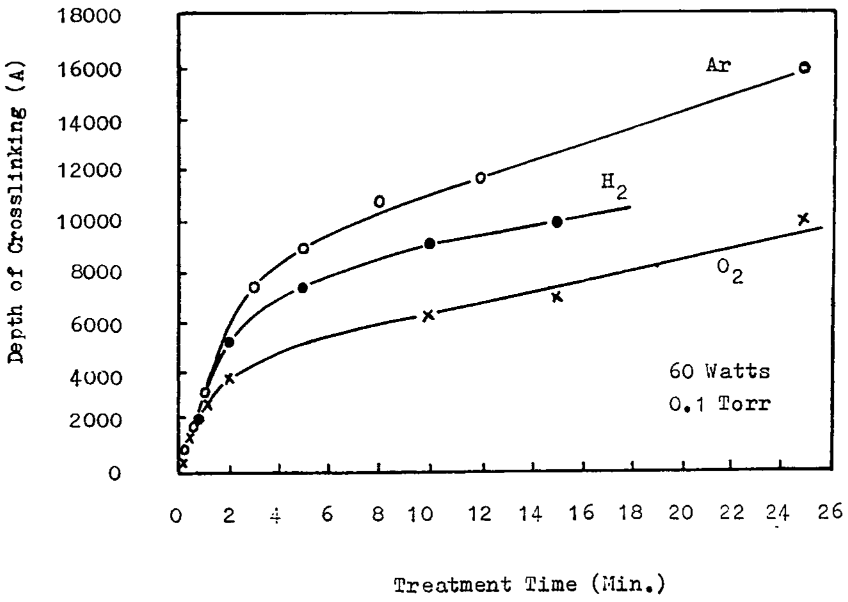

Figure 2 Depth of cross-linking as a function of exposure time in different treatment gases at 60 W, 0.1 Torr.

as the sample is exposed to the glow discharge, and the thickness of the cross-linking layer increases with the treatment time and can reach a rather great scale,[7] as it is shown in Figure 2. Because the penetrating ability of the active species of the plasma is relatively low, it is obvious that the cross-linking density will decrease with the depth gradually. Table I lists the data of the elemental analysis of the gel. It indicates that the average cross-linking degree induced by plasma is very low and can be neglected compared to those of the plasma-polymerized polymer (the ratio of H/C is about 1.49/1 in the plasma polyethylene[12]). The result of the elemental analysis also demonstrates that the contents of the oxygen and nitrogen in the gel cannot be detected. It implied that the oxygen and nitrogen are not obviously introduced into the cross-linking layer during the plasma treatment. This was further supported by the infrared analysis results, as shown in Figure 3. The infrared spectra of the gel show that no new absorption can be observed in the gel and the primary absorptions of the HDPE at 2846 cm^{-1} (CH_3 and $-CH_2-$ stretching), 1465 cm^{-1} (CH_3 and $-CH_2-$ bending), 1373 cm^{-1} (CH_3 bending), 1303 cm^{-1} ($-CH_2-$ bending), and 723 cm^{-1} ($(-CH_2-)_n$ bending) remain unchanged in both the peak strengths and wavenumbers after treatment. On the other hand, the ESCA study of the treated

Table I The Element Constitutions of the Gels and the Surface of the Treated HDPE

Treatment Conditions[a]	Cross-linking Depth (Å)	Element Constitutions of the Gel (Elemental Analysis)					Element Constitutions on the Surface (ESCA)	
		H	C	N	O	H/C	O/C	N/C
Untreated HDPE	—	33.5	66.5	—	—	1.985	0.052	—
150 w, 60 min.	21,446	33.3	66.7	—	—	2.000	0.165	0.024
150 w, 15 min	12,461	33.4	66.6	—	—	1.994	0.159	0.024
150 w, 2 min	9,365	33.7	66.3	—	—	1.967	0.113	0.023

[a] Ar pressure 0.1 Torr.

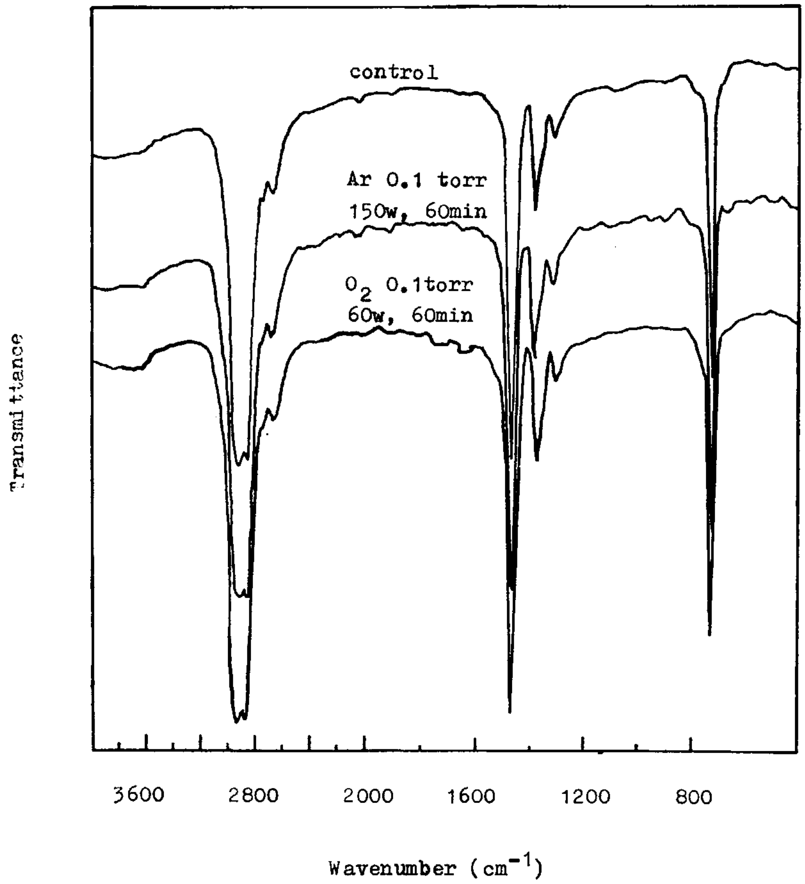

Figure 3 IR spectra of the cross-linking layer of HDPE treated at 150 W, 15 min, 0.1 Torr.

HDPE has proved that on the surface of the treated sample there is much higher O/C and N/C ratios than those of the control,[9] as shown in Table I. The above results indicate that the polar groups introduced by plasma just locate in the supersurface of the HDPE. The chemical constitution and structure of the inner part of the cross-linking layer are not affected, except for being slightly cross-linking.

Figures 4 and 5 show the X-ray diffraction and the DSC curves of the cross-linking layer. Figure 4 also shows that the crystal configuration in the cross-linking part is the same as that of the uncross-linking HDPE, but the crystallinity, as shown in the last column of Table II, is much lower than that of the untreated sample. We can obtain more information about the thermal behavior of the gel from Figure 5. Figure 5(a) shows that the crystal melt point of the cross-linking part shifts from 405 to about 399.5 K and the peaks of melting become much wider than those of the untreated HDPE. Additionally, the crystallization exothermal curves of the treated HDPE are demonstrated in Figure 5(b). The untreated HDPE has a sharp crystal exothermal peak in 384.8 K, but all the treated samples have double peaks. One is still located at about 384.5 K, and the other appears at 381 K. The changes of the treatment conditions have no influence on these peak temperatures.

These results indicate that because the mobility of the molecules in the gel is limited by the cross-linking bonds and the regularity of the molecules is spoiled by these bonds the crystallization becomes difficult and the crystallinity becomes imperfect. The results also imply that the crystallization of the treated HDPE is performed in two different processes: When the cross-linking degree of the molecules reaches a certain extent, the crystallization temperature will shift from 384.5 to about 381 K. In other words, the peak appearing at 384.5 K represents the crystallization of the molecules that have high mobility similar to that of the uncross-linking molecules, and the peak at 381 K represents that of

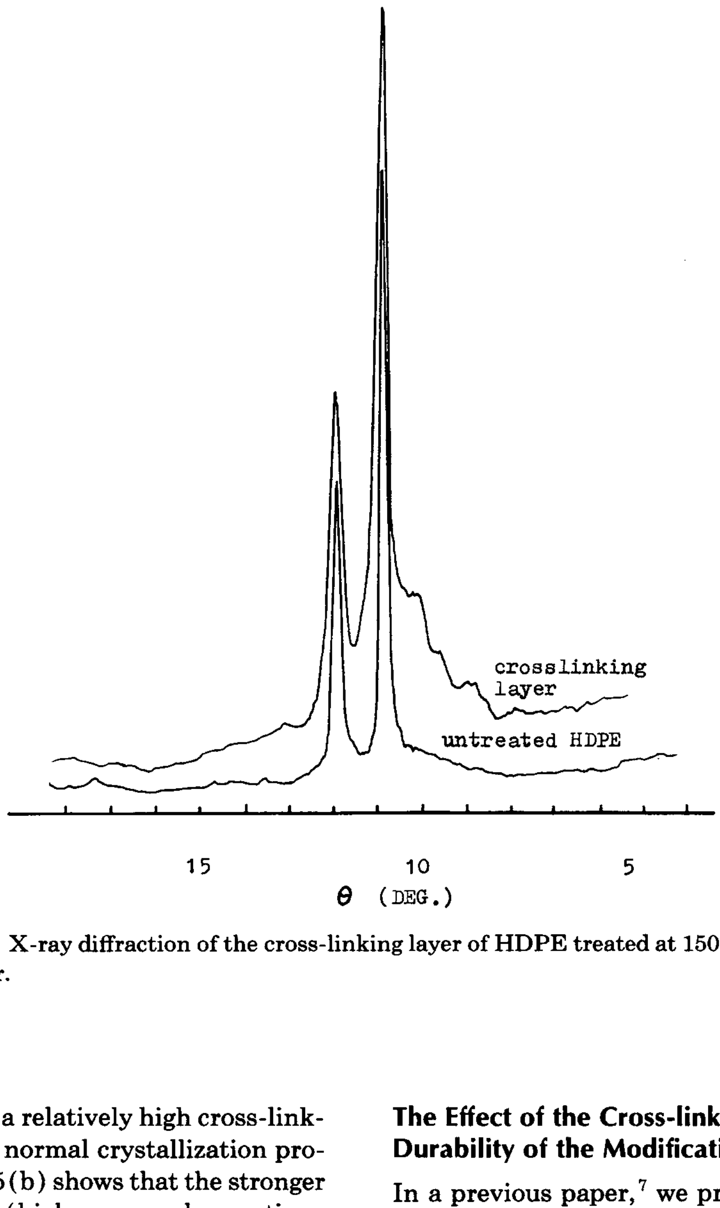

Figure 4 X-ray diffraction of the cross-linking layer of HDPE treated at 150 W, 60 min, Ar 0.1 Torr.

the molecules that have a relatively high cross-linking degree in which the normal crystallization process is hindered. Figure 5(b) shows that the stronger the treatment condition (higher power, longer time, etc.) the higher the peak at 381 K, i.e., the greater the ratio of high cross-linking degree. Based on this postulation, the relationships between the cross-linking density of the molecules and the crystallization temperature as well as the ratio of the two different crystallization processes are schematically shown in Figure 6.

Some of the thermal behavior and the crystallinity data are listed in the Table II. There is no obvious difference among the crystallinities of the gels obtained in different treatment conditions that lead to great differences in both the thickness of the cross-linking layer and the cross-linking structure. This seems to be a unified result of the variety of the cross-linking gradient in the gels.

The Effect of the Cross-linking Layer on the Durability of the Modification Efficiency

In a previous paper,[7] we proved that the improvement of the surface energy of HDPE in the plasma treatment are basically not due to the surface cross-linking, and the surface energy of the HDPE will reach its maximium and remain constant after 1 min of treatment. Nevertheless, it is well known that the modification efficiency of the polymers introduced by plasma treatment decays with the aging time. Figures 7 and 8 show the decay of the surface energies of HDPE treated by different conditions. It can be noticed that, even though the modification efficiencies obtained in different treatment conditions are quite similar before aging, their decay rates depend remarkably on the treatment conditions. The entire decay process can be approximately divided into two parts: The first part covers a few days and has a much higher decay rate than that of the

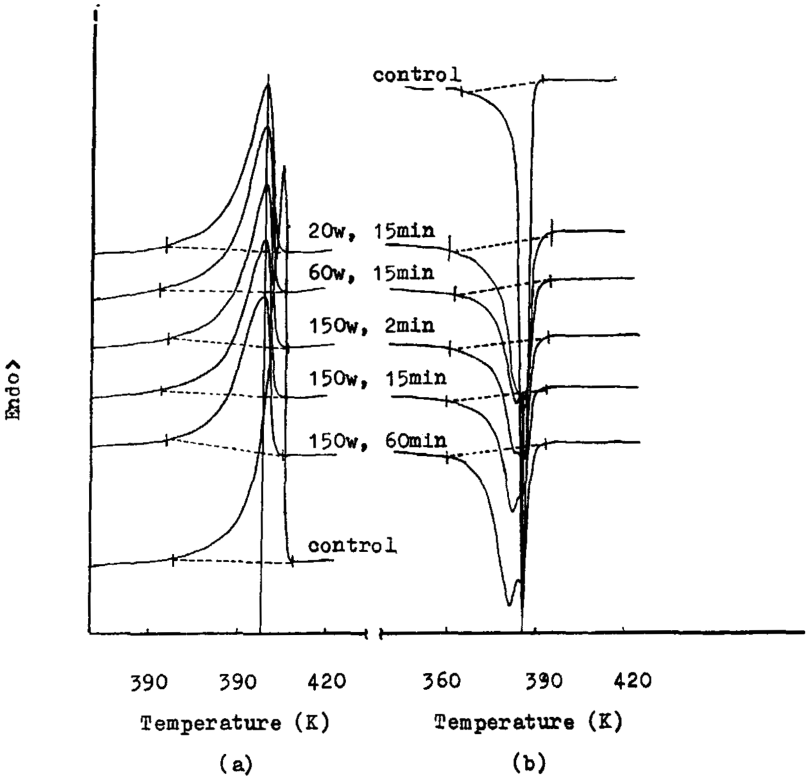

Figure 5 DSC curves of the cross-linking layer as a function of the treatment conditions.

second part, and most of the decay of the surface energy is in this part. The decay rate in the second part is very slow and the surface energy eventually approaches a constant in about 1 month. For comparison of the decay rates of surface energies of HDPE with different cross-linking thicknesses, the decay rate in the first part was taken to represent the decay rate of the treated HDPE. Then, the decay rate K can be formulated as the following:

$$K = \frac{r - r_1}{(r - r_0)^D}$$

Additionally, the decay value in 45-day storage was taken to represent the total decay value of the sample, i.e.:

$$\text{Total decay value } T = \frac{r - r_2}{r - r_0}$$

where r, r_1, r_2, and r_0 are the surface energies measured immediately after the treatment, in the turning point of the curve, after 45-day storage, and in the untreated HDPE, respectively; D is the aging time at the turning point (days), as demonstrated in Figure 7.

Figure 9 shows the plot of the decay rates and the total decay value of the surface energy vs. the cross-

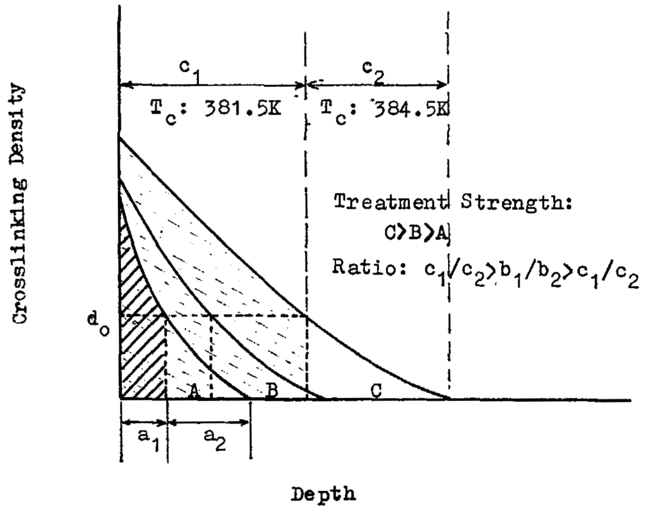

Figure 6 Relationship between cross-linking density and crystallization temperature of HDPE.

Table II Thermal Properties and Crystallinity of the Cross-linking Layer

Treatment Conditions	Cross-linking Depth (Å)	Melting Point	Crystallization					Crystalline Grade (X-ray)
			St[a]	Max[a]	End[a]	Span[a]	Δ*H*[b]	
Control	/	405.8	362.7	385.3	391.4	28.7	−38.79	67%
Control′[c]	/	405.0	362.9	384.4	390.6	27.7	−38.72	71%
150 W, 60 min	21446	399.6	358.1	381.0	393.9	35.8	−25.56	60.2%
150 W, 15 min	12461	399.5	358.7	381.7	392.4	33.7	−23.60	59.9%
150 W, 2 min	9365	399.7	359.2	384.4	392.4	33.2	−23.06	60.4%
60 W, 15 min	11282	399.6	360.0	381.0	392.4	32.4	−23.80	58.6%
20 W, 15 min	7334	399.5	358.7	384.7	393.9	35.2	−23.70	57.2%

[a] Temperature (°C).
[b] Cal/gram.
[c] Soluble part of the treated HDPE.

linking thickness. The cross-linking induced by plasma treatment can efficiently hinder the decay process. The thicker the cross-linking layer, the slower the decay rate and the lower the total decay value. The cross-linking caused by different treated gas has obviously a different effect on the decay process. The cross-linking caused by O_2 plasma is much more efficient in hindering the decay than those of the H_2 and Ar plasma. Although Ar plasma is the most efficient gas to cause cross-linking of the HDPE in the above three gases,[7] its cross-linking layer is the most inefficient in hindering the decay process among them. Figure 10 demonstrates the dependence of the surface energy of the HDPE and its decay rate in aging on the plasma treatment time. This figure indicates that, even though the modification efficiency will reach its highest equilibrium value in not more than 1 min of treatment, its decay is very fast in such a short treatment time. With further increase of the treatment time, the surface energy will not change any more, but its durability increases remarkably (the decay rate of the treat-

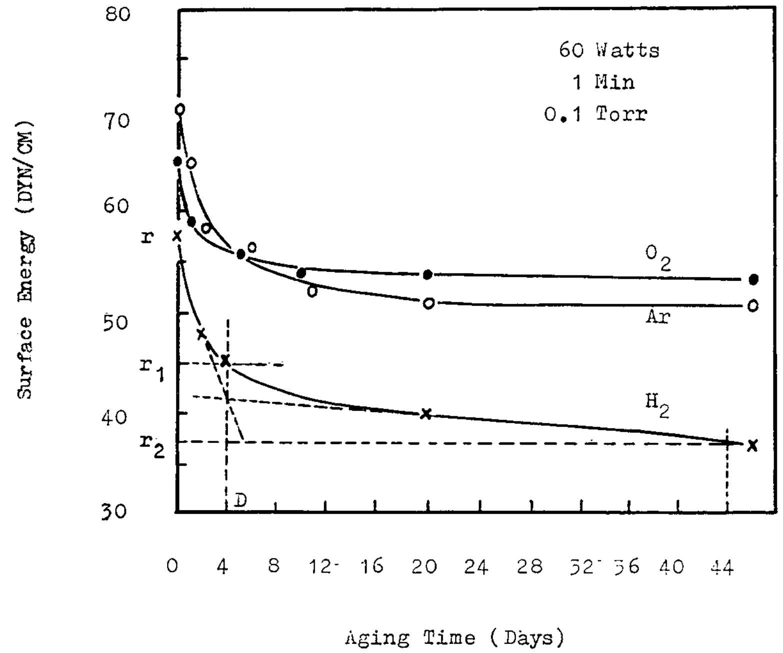

Figure 7 Decay of the surface energy of HDPE treated in different gases with aging.

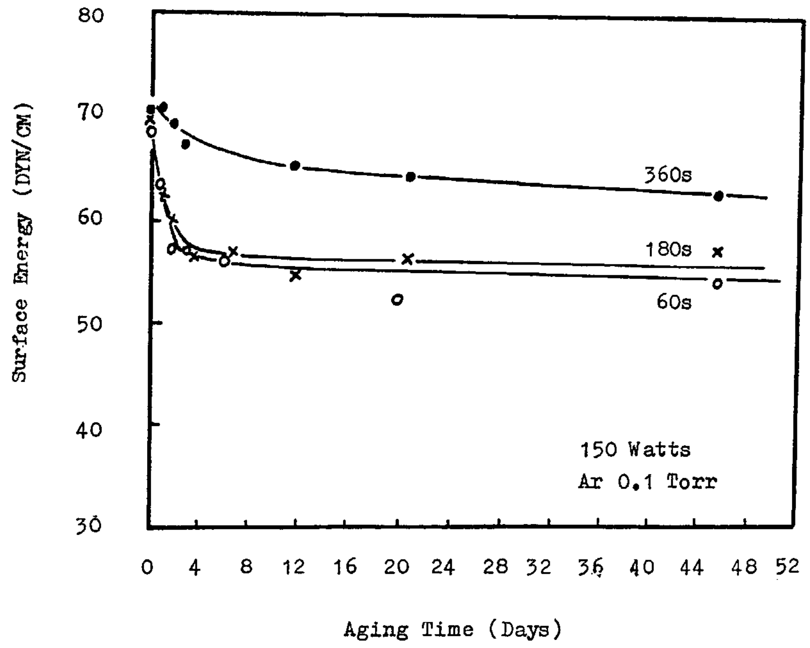

Figure 8 Decay of the surface energy of HDPE treated for different lengths of time with aging.

ment efficiency decreases rapidly). After a certain extent of treatment, the change of the decay rate turns to slow and then approaches the equilibrium. It is also noticed in Figure 10 that, from the viewpoint of the treatment time, the O_2 plasma is also most efficient in obtaining a durable modification efficiency than is H_2 and Ar. This result seems to indicate that the cross-linking layer induced by O_2 plasma has higher surface cross-linking density and therefore it is more efficient in hindering the rotation and burying of the polar groups, but this explanation should be further tested by experiment.

Because the cross-linking layer of HDPE induced by plasma treatment can hinder the decay of the

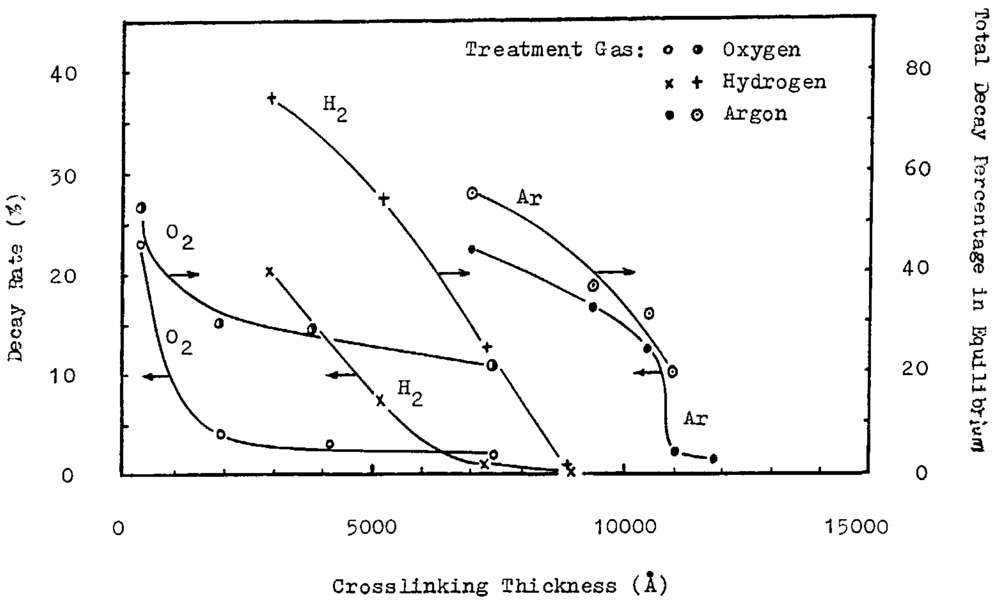

Figure 9 Relationships between the cross-linking thickness and the decay rate and total decay value of surface energy.

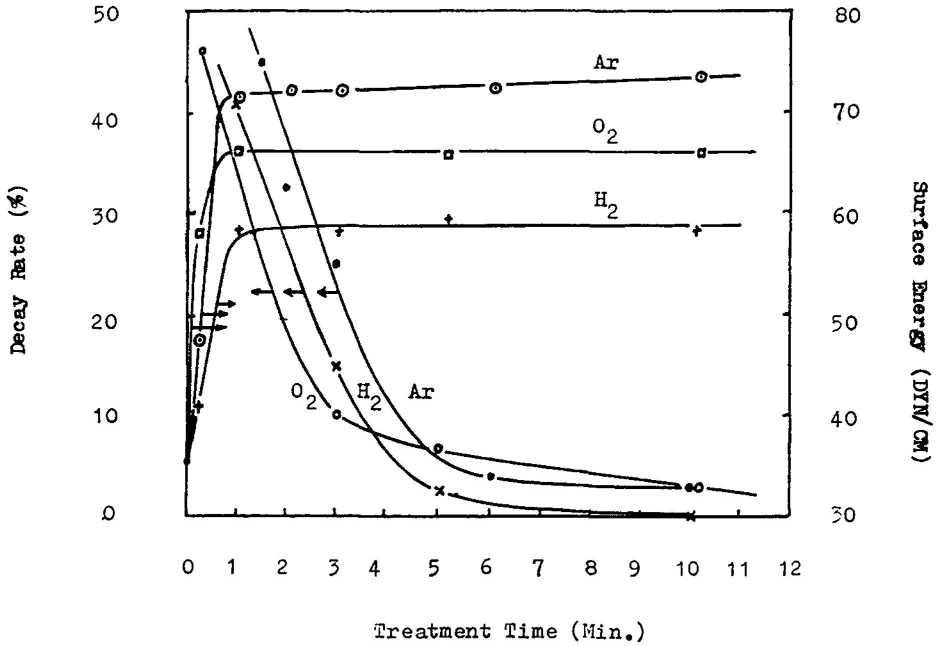

Figure 10 Surface energy and its decay rate as function of treatment time.

surface energy, it is believed that, although the average cross-linking degree of the gel is very low, the cross-linking density of the upper surface molecules is quite high and therefore the mobility of the molecules and the rotation of the polar groups are prevent by these cross-linking bonds. As a result, the modification efficiency provided by the plasma treatment can be maintained for a long time because the polar groups introduced by the plasma constantly stay on the surface of the HDPE.

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