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Effect of ageing atmospheres on the changes in surface free energies of oxygen plasma-treated polyethylene films

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Abstract: The changes in the surface properties of oxygen plasma-treated polyethylene films during ageing in various atmospheres (water, dry nitrogen gas, and hexane) were studied from the viewpoint of the interaction of the surface functional groups formed on the films and the ageing media. The XPS (x-ray photoelectron spectroscopy) and the SSIMS (static secondary ion mass spectrometry) spectra indicated the formation of polar groups containing oxygen such as C=O on the film surface. The changes in the critical surface tension (γ_C) of the film with ageing time were largely affected by the ageing atmospheres: the γ_C value of the film aged in water increased, and those of the films aged in nitrogen gas and hexane decreased with an increase in ageing time. These different tendencies among the ageing media could be understood reasonably with examining the surface free energy ratios (the total energy, γ_S^{tot}; the dispersion force component, $\gamma_S^d/\gamma_S^{tot}$; the polar component, $\gamma_S^p/\gamma_S^{tot}$; the hydrogen bonding component, $\gamma_S^h/\gamma_S^{tot}$) of the films. The ageing in water of which γ_L is large gave the films with higher $\gamma_S^p/\gamma_S^{tot}$ values, suggesting that the overturn and/or the orientation of the polar groups toward the water phase occurred so as to minimize the discrepancy of the surface free energy between the polymer surface and water. On the other hand, the ageing in nitrogen gas and hexane media of which γ_L are small gave the films with lower $\gamma_S^p/\gamma_S^{tot}$ and $\gamma_S^h/\gamma_S^{tot}$ values, suggesting the overturn and/or the orientation of the polar groups into the bulk polymer.

Key words: LLDPE film – oxygen plasma treatment – SSIMS analysis – critical surface tension – surface free energy

1. Introduction

It is well known that the surface properties of a polymer are greatly affected by functional groups formed on its surface [1–5]. In our previous paper, we described that the surface properties of copolymer plates prepared by copolymerization of styrene (St) and acrylic acid (AA) depended on the materials of used frames contacted with reaction system during the polymerization, and that the surface free energy of the prepared plates reflected the orientation of the functional groups on their surface [6].

In addition, the surface properties of polymeric materials are also affected by their histories, ageing environments, and so on. An early study reported by Baszkin and co-workers showed that the wettabilities of the chemically oxidized polyethylene films changed depending on the ageing temperature [7]. Recent attention has been paid to dynamic surface properties of plasma-treated polymeric materials. For example, Yasuda et al. studied the changes in wettabilities of glow-discharge-polymerized polymers prepared by oxygen plasma treatment [8]. Morra and coworkers reported on the recovery process of hydrophobic property of oxygen plasma-treated poly(dimethylsiloxane) during ageing in air and water [9]. These authors suggested that the overturn and the migration of the surface functional groups were responsible for the changes in their surface properties. These behaviors of the functional groups, however, are merely described phenomenologically, and the driving force inducing these changes in the functional groups remains ambiguous.

The contact angle of a solid essentially reflects the topmost surface property, and can be used to estimate its critical surface tension (γ_C). We reported, however, that the critical surface tension was insufficient for the elucidation of the changes in the functional groups, and their changes could be thermodynamically clarified by use of the surface free energy [6].

Thus, we have been concerned about the estimation of the changes in the properties of the oxygen plasma-treated linear low density polyethylene (LLDPE) films during ageing in various atmospheres with the aid of the thermodynamically well-defined surface free energy (γ_S^{tot}) and its components (the dispersion force component, γ_S^d; the polar component, γ_S^p; the hydrogen bonding component, γ_S^h).

In this study, the plasma-treated LLDPE films were aged in various media with different surface free energies, namely, water, dry nitrogen gas, and hexane. The changes in the surface free energies of the LLDPE films are discussed from the viewpoint of the interaction of the surface functional groups formed on the LLDPE films and the used media.

2. Experimental

2.1. Materials and oxygen plasma treatment

Linear low density polyethylene films (LLDPE; thickness 100 μm; M_n, 26700; M_w, 81700; M_w/M_n, 3.06) used for this study were kindly supplied by Idemitsu Petrochemical Co., Ltd. The LLDPE films were washed with methanol in a soxhlet extractor for 48 h and dried under reduced pressure.

Oxygen plasma treatment was performed using a parallel plate reactor (BP-1, Samco International CO., Ltd.). The plasma parameters were the following: excitation frequency, 13.56 MHz; power, 10 W; pressure, 20 Pa; gas flow, 20 ml/min; treatment time, 1 min. The LLDPE films were used in the form of 20 × 40 mm stripes.

The plasma-treated samples were aged in various atmospheres: distilled water, dry nitrogen gas, and hexane, for certain periods of time at 20 °C. Before the contact angle measurements, the samples aged in water were briefly washed with distilled methanol and dried under reduced pressure at room temperature. Those which were aged in hexane were only dried under reduced pressure at room temperature.

2.2. Contact angle measurement

Contact angles were evaluated with distilled water, glycerol, formamide, thiodiglycol, ethyleneglycol, methylene iodide, tetrabromoethane, 1-bromonaphthalene, and tricresyl phosphate. The liquids except water were commercially available (Wako Pure Chemical Ind., Co., Ltd.) and were used without further purification. Contact angles (sessile drop method) were measured by use of a contact angle meter (CA-D, Kyowa Interface Science Co., Ltd.) at 20 °C in an air-conditioned room.

2.3. XPS and SSIMS analyses

XPS (x-ray photoelectron spectroscopy) and SSIMS (static secondary ion mass spectrometry) analyses were performed using a Perkin-Elmer PHI MODEL 5500MT ESCA/SIMS instrument. XPS spectra were obtained with a monochromatic Al K_α x-ray source at 150 W. SSIMS analysis of the plasma-treated samples was normally performed c. 4 weeks after the plasma treatment. The measurement conditions were as follows: ion bombardment was 3 KeV Xe^+ at a current density of 1 nA/cm^2, an acquisition time was 1.67 min, and charge neutralization of the samples was accomplished using a low energy ($\sim$10 eV) electron flood.

2.4. Estimation of critical surface tension and surface free energy

The critical surface tension of wetting (γ_C) was defined by the value to which the surface tension of the wetting liquid (γ_L) is extrapolated, as the cosine of the contact angle, cos θ, tends to unity on a Zisman plot, the plot of cos θ vs. γ_L [10–12].

The Young equation relating the tensions at the three-phase contact point to the equilibrium contact angle, θ, may be written as:

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta \, , \tag{1}$$

where γ_{SL} indicates the tension at the solid/liquid point.

When $\cos\theta \to 1$, $\gamma_L \cong \gamma_C$ and $\gamma_{SL} = \gamma_{SL}^*$. Then, Eq. (1) is transformed as:

$$\gamma_C = \gamma_S - \gamma_{SL}^* , \qquad (2)$$

where

θ: contact angle (deg.);
γ_C: critical surface tension (mJ/m^2);
γ_L: surface free energy of liquid (mJ/m^2);
γ_S: surface free energy of solid (mJ/m^2);
γ_{SL}: interfacial free energy between solid and liquid (mJ/m^2).

It should be noted here that γ_C is evidently not equal to γ_S.

The surface free energy and its components of the LLDPE films were calculated using Eqs. (3) and (4) [13]:

$$\gamma_L(1+\cos\theta) = 2(\gamma_S^d\gamma_L^d)^{1/2} + 2(\gamma_S^p\gamma_L^p)^{1/2} + 2(\gamma_S^h\gamma_L^h)^{1/2} \qquad (3)$$

$$\gamma^{tot} = \gamma^d + \gamma^p + \gamma^h , \qquad (4)$$

where the superscripts indicate the followings, respectively:

d: the dispersion force component of surface free energy;
p: the polar component of surface free energy;
h: the hydrogen bonding component of surface free energy.

Contact angles were measured with nine kinds of liquids of which components of the surface free energy are known [13]. Optimal solution for γ_S^d, γ_S^p, and γ_S^h was obtained by applying a nonlinear least square method (Marquartdt method) to Eq. (3).

3. Results and discussion

3.1. XPS and SSIMS analyses

XPS C_{1s} spectra of the original and the plasma-treated LLDPE film are shown in Fig. 1. A single peak assigned as $-\!(\underline{C}H_2\text{-}CH_2)\!-_n$ is observed at 285.0 eV in the original spectrum (b). Broad peaks are observed beside the strongest peak in the treated film (a). These peaks are separated to 286.9 and 289.0 eV by Gaussian function, and are normally assigned to –OH and C=O, respectively.

A negative ion SSIMS spectrum of the original LLDPE film showed the characteristic peaks at mass 13 and 25 (CH^- and C_2H^-, respectively), and was in good agreement with that reported in the literature [14]. The new peaks at mass 16 and 17 which were assigned to O^- and OH^-, respectively, were observed in the spectrum of the plasma-treated film.

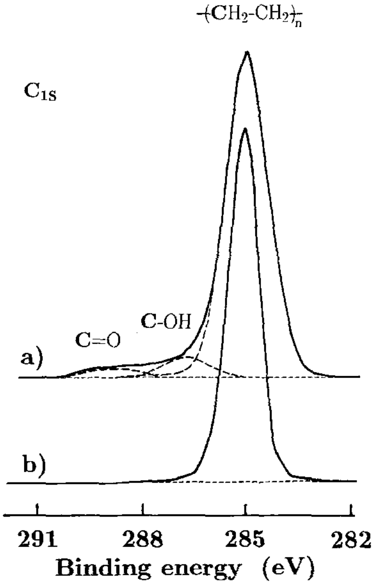

Fig. 1. C_{1s} XPS spectra of LLDPE. a) Plasma-treated LLDPE; b) Original LLDPE.

The positive ion SSIMS spectrum of the original LLDPE was also in good agreement with that reported in the literature [14]. Most of the positive ion SSIMS peaks were assigned to $C_nH_{2n+1}^+$ and $C_nH_{2n-1}^+$. The 0–100 amu range was dominated mainly by peaks at mass 15 (CH_3^+), 29 ($C_2H_5^+$), 43 ($C_3H_7^+$), 55 ($C_4H_7^+$), and 69 ($C_5H_9^+$).

The relationship between the carbon number, n, and the cumulative positive ion intensity of LLDPE is shown in Fig. 2. The plasma treatment increases the intensities of the positive ions of the species with relatively small n values. Especially, remarkable increase is observed in $n = 3$ and $n = 4$. The results apparently reveal that the polymer surface is damaged by the plasma treatment.

3.2. Critical surface tension

The relationship between ageing time and the γ_C value of the LLDPE film is shown in Fig. 3. The γ_C value of the LLDPE film increases remarkably by the plasma treatment from 26.3 to 45.9 mJ/m^2, indicating the introduction of the

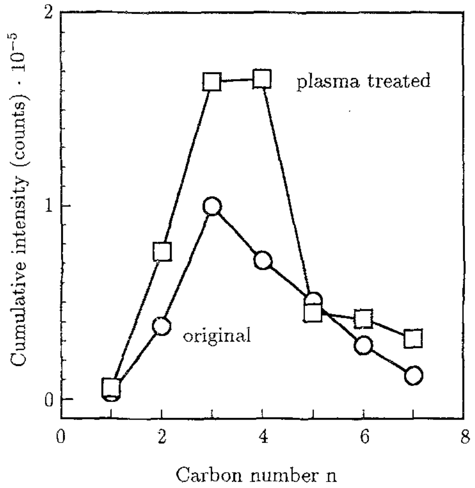

Fig. 2. Relationship between carbon number n and cumulative positive ion intensity of LLDPE.

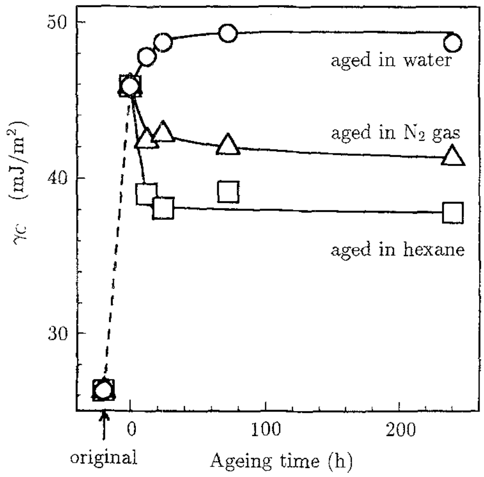

Fig. 3. Relationship between ageing time and γ_C value of plasma-treated LLDPE aged in various atmospheres at 20 °C.

hydrophilic property on the film surface. However, the attained γ_C value changes remarkably with ageing time, and the extent of the change is largely affected by the exposed atmosphere.

In the case of the film aged in water, the γ_C value of the plasma-treated sample increases with ageing time within c. 24 h and then levels off. On the contrary, in the case of the films aged in nitrogen gas and hexane, the γ_C value of the plasma-treated sample decreases rapidly after c. 24 h from 45.9 to 42.8, and to 38.1 mJ/m^2, respectively.

The fact mentioned above suggests that the surface properties of the plasma-treated samples are influenced by the exposed media during ageing. The γ_C value, however, is only a critical value for the complete wetting, that is, a liquid with γ_L could wet a solid perfectly when $\gamma_C > \gamma_L$. The behavior of the γ_C values in Fig. 3, therefore, could not reveal what changes occur on the polymer surface, and the γ_C values seem insufficient for the further discussion.

In this context, Zisman already pointed out that γ_C does not directly represent the surface free energy (γ_S) of the material (see Eq. (2)). The solution of this problem could be given by the concept of the surface free energy proposed by Fowkes. He first proposed that the surface free energy of a pure phase could be represented by the sum of the contributions arising from different types of surface force components [15, 16]. Owens [17], Dann [18], and Schwarcz [19] supported the Fowkes's concept to estimate the components of the surface free energy for several polymers.

As mentioned above, the plasma treatment introduces the polar functional groups such as carbonyl, hydroxyl group, and so on which lead the formation of the polar–polar interaction and the hydrogen bonding on the polymer surface. Therefore, it is of use to apply Hata's method [13] for this system. He suggested that the surface free energy could be expressed by three terms, namely, a dispersion force (γ_S^d), a polar (γ_S^p), and a hydrogen bonding component (γ_S^h). Therefore, detailed discussion will be made in the following section using the extended Fowkes's equation by Hata.

3.3. Surface free energy and its components

Total surface free energy: The relationship between ageing time and the γ_S^{tot} values of the LLDPE films aged in water, nitrogen gas, and hexane are shown in Fig. 4.

The γ_S^{tot} value of the original film increases from 32.3 to 48.4 mJ/m^2 by the plasma treatment. For the increase in the γ_S^{tot} value, however, one must take into consideration a possible introduction of a roughness on the polymer surface by the plasma treatment, which affects the contact angles. A slight increase of the roughness was actually observed by SEM.

Figure 4 indicates that the γ_S^{tot} value of the plasma-treated sample increases with ageing time

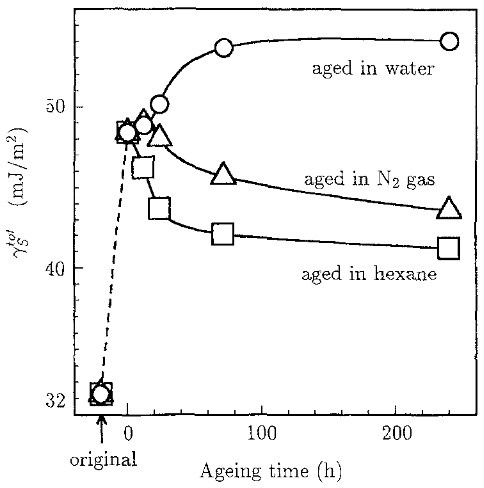

Fig. 4. Relationship between ageing time and $\gamma_{\mathrm{S}}^{\mathrm{tot}}$ value of plasma-treated LLDPE aged in various atmospheres at 20 °C.

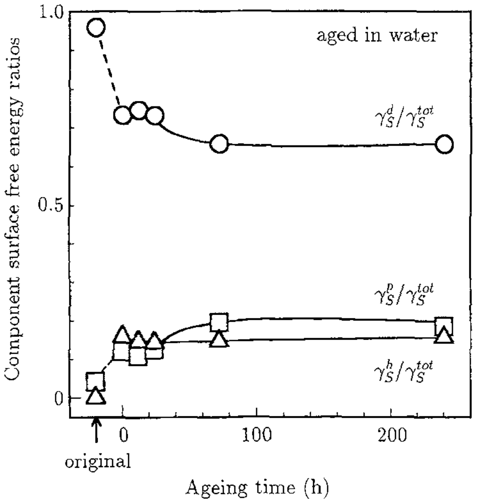

Fig. 5. Relationship between ageing time and component surface free energy ratios of plasma-treated LLDPE aged in water at 20 °C.

in the case of the films aged in water, while it decreases with ageing time for the films aged in nitrogen gas and hexane. The decreasing of the $\gamma_{\mathrm{S}}^{\mathrm{tot}}$ value in hexane is larger than that in nitrogen gas.

The relationships between the ageing time and the component surface free energy ratios against the total surface free energy ($\gamma_{\mathrm{S}}^{\mathrm{d}}/\gamma_{\mathrm{S}}^{\mathrm{tot}}$, $\gamma_{\mathrm{S}}^{\mathrm{p}}/\gamma_{\mathrm{S}}^{\mathrm{tot}}$, and $\gamma_{\mathrm{S}}^{\mathrm{h}}/\gamma_{\mathrm{S}}^{\mathrm{tot}}$) of the LLDPE aged in water, nitrogen gas, and hexane are shown individually in Figs. 5–7. These ratios could neglect the influences of the roughness against the contact angle.

Ageing in water: As shown in Fig. 5, in the case of the films aged in water, the $\gamma_{\mathrm{S}}^{\mathrm{d}}/\gamma_{\mathrm{S}}^{\mathrm{tot}}$ ratio, 0.96 for the original film, decreases to 0.72 by plasma treatment, and the ratio decreases with ageing time. The $\gamma_{\mathrm{S}}^{\mathrm{p}}/\gamma_{\mathrm{S}}^{\mathrm{tot}}$ ratio, 0.04 for the original film, increases to 0.12 by the plasma treatment, and the ratio increases with ageing time. The $\gamma_{\mathrm{S}}^{\mathrm{h}}/\gamma_{\mathrm{S}}^{\mathrm{tot}}$ ratio also increases from 0.00 to 0.16, but the ratio keeps constant (0.16) in spite of increasing in ageing time.

The increase in the $\gamma_{\mathrm{S}}^{\mathrm{tot}}$ value by the plasma treatment is mainly due to the increase in the polar and the hydrogen bonding components, and the dispersion force component affects conversely.

The fact that the $\gamma_{\mathrm{S}}^{\mathrm{tot}}$ values of the plasma-treated samples increase with ageing time could be understood as the result of an optimization of the interfacial free energy between water ($\gamma_{\mathrm{water}} = 72.8$ mJ/m^2) and the plasma-treated sample ($\gamma_{\mathrm{S}}^{\mathrm{tot}} = 48.4$ mJ/m^2). The increase in the polar component of the surface free energy during ageing suggests an orientation of the polar functional groups toward the water phase, while the constant ratios of the hydrogen bonding component ($\gamma_{\mathrm{S}}^{\mathrm{h}}/\gamma_{\mathrm{S}}^{\mathrm{tot}}$) indicate that the component is rapidly optimized and attained a constant value when immersed in water.

Ageing in nitrogen gas and hexane: In the case of the films aged in nitrogen gas and hexane, the changes in the surface free energy are quite different. The $\gamma_{\mathrm{S}}^{\mathrm{tot}}$ values of the plasma-treated samples decrease with ageing time (see Fig. 4), and as shown in Figs. 6 and 7, the $\gamma_{\mathrm{S}}^{\mathrm{d}}/\gamma_{\mathrm{S}}^{\mathrm{tot}}$ ratios increase with ageing time, while the $\gamma_{\mathrm{S}}^{\mathrm{p}}/\gamma_{\mathrm{S}}^{\mathrm{tot}}$ and $\gamma_{\mathrm{S}}^{\mathrm{h}}/\gamma_{\mathrm{S}}^{\mathrm{tot}}$ ratios decrease.

However, these behaviors seem reasonable considering that the optimization of the interfacial free energy occurs ($\gamma_{\mathrm{hexane}} = 18.4$ mJ/m^2). The decreases in the polar and the hydrogen bonding components suggested that the polar functional groups orient toward the bulk polymer contrary to the films aged in water.

The $\gamma_{\mathrm{S}}^{\mathrm{tot}}$ value of the film aged in hexane are smaller than those of the films aged in nitrogen gas, while the $\gamma_{\mathrm{S}}^{\mathrm{d}}/\gamma_{\mathrm{S}}^{\mathrm{tot}}$ ratios in the hexane series are larger than the nitrogen gas series. The $\gamma_{\mathrm{S}}^{\mathrm{p}}/\gamma_{\mathrm{S}}^{\mathrm{tot}}$ and $\gamma_{\mathrm{S}}^{\mathrm{h}}/\gamma_{\mathrm{S}}^{\mathrm{tot}}$ ratios in the hexane series are smaller than the nitrogen gas series.

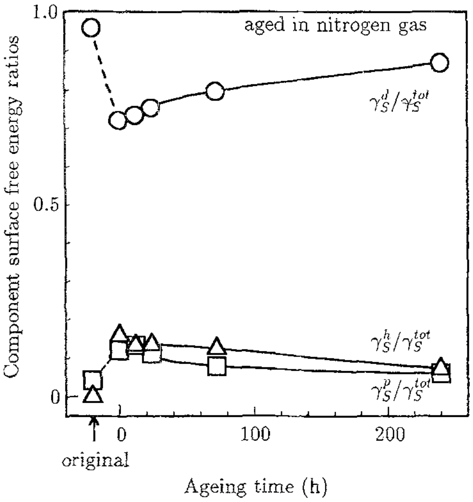

Fig. 6. Relationship between ageing time and component surface free energy ratios of plasma-treated LLDPE aged in nitrogen gas at 20 °C.

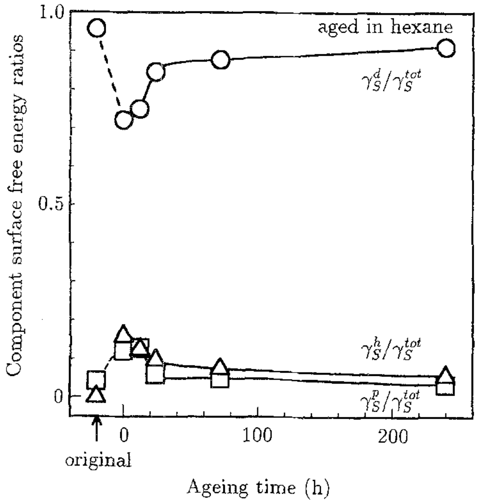

Fig. 7. Relationship between ageing time and component surface free energy ratios of plasma-treated LLDPE aged in hexane at 20 °C.

The extent of the changes in the component surface free energy ratios for the films aged in nitrogen gas differ from those in hexane. Namely, the ratio of the film aged in nitrogen gas decreases slowly with ageing time. On the other hand, the ratio for the film aged in hexane decreases rapidly at the beginning of the ageing and slowly afterward.

Since it could be assumed that $\gamma_{\mathrm{nitrogen}} = 0$, or at least $\gamma_{\mathrm{nitrogen}} < \gamma_{\mathrm{hexane}}$, the surface free energy ratios of the nitrogen gas series were expected to change rapidly and become smaller than those of the hexane series. This prediction, however, did not agree with the experimental results. The inconsistency probably arose from the increase in the mobility of the chain molecules in the interface due to a partial solvation of hexane molecules to the polymer segments.

4. Conclusion

The oxygen plasma treatment introduced the polar functional groups such as C=O onto the LLDPE film surface, resulting in an increase in the surface free energy (γ_S^{tot}). The γ_S^{tot} values were strongly influenced by the surface free energy of the successively exposed atmospheres, namely, water, dry nitrogen gas, and hexane.

In the case of the films aged in water having high surface free energy, the γ_S^{tot} value of the plasma-treated film increased with ageing time. The increase in the γ_S^{tot} value was attributed to that in the polar component and to the corresponding decrease in the dispersion force component. The polar ($\gamma_S^{\mathrm{p}}/\gamma_S^{\mathrm{tot}}$) and the hydrogen bonding ($\gamma_S^{\mathrm{h}}/\gamma_S^{\mathrm{tot}}$) component ratios were larger than those of the films aged in the low free energy's atmospheres. In spite of the increase in the polar component, however, the contribution of the dispersion force component to the surface free energy was the largest among the three components.

The results suggested that the polar functional groups on the surface reoriented in order to optimize the γ_S^{tot} value, that is, the disorderly polar functional groups introduced by the plasma treatment oriented toward the water phase, resulting in the increase in the γ_S^{tot} values.

On the other hand, the γ_S^{tot} values of the plasma-treated films aged in nitrogen gas and hexane having low surface free energy decreased with ageing time. The decrease in the γ_S^{tot} value indicated the disappearance of the polar functional groups on the surface by the overturn and/or the orientation resulting from the optimization of the interfacial free energy.

Despite that the optimization proceeded, however, the polar and the hydrogen bonding components were still observed on the films aged for a long time in the media with the low free energy. The overturn and orientation of the polar groups, therefore, would occur in the relatively thin layer of the polymer surface.

As mentioned above, the optimization of the surface free energy could be clarified by the estimation of the individual component surface free energies (the dispersion force component, γ_S^d; the polar component, γ_S^p; and the hydrogen bonding component, γ_S^h) of the films.

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