Formation of Conjugated Carbon Bonds on Poly(vinyl chloride) Films by Microwave-Discharge Oxygen-Plasma Treatments

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ABSTRACT: Conjugated polyene bonds on poly(vinyl chloride) (PVC) films were rapidly formed by the treatment of oxygen plasma produced by microwave discharge. Changes affecting the formation of conjugated carbon bonds on PVC were studied with respect to plasma emission diagnostic and surface properties of the film with fluorescence, refractant absorption spectroscopy, X-ray photoelectron spectroscopy analysis, and Raman spectroscopy. The formation of polyene bonds on the film surface was responsible for both the dechlorination and dehydrogenation of PVC in the plasma atmosphere. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 589–594, 2005

Key words: poly(vinyl chloride) (PVC); modification; surfaces

INTRODUCTION

Plasma techniques are useful and effective in improving the surface properties of polymers.[1,2] It is often desirable to modify the properties of a polymer surface without affecting the characteristics of the bulk polymer material. Therefore, these techniques have been extensively used in a wide variety of polymer applications. Through plasma treatment and plasma polymerization,[3–5] polymer properties such as abrasion resistance,[6] selective separation performance,[7] wettability, and affinity to biological substances[8,9] have been significantly improved.

Microwave plasma has been used conventionally for the surface modification of polymer films.[10–13] We are interested in plasma produced by microwave discharge because of the useful applications of the excited species in plasma available for the simultaneous treatment of polymer surfaces in a plasma atmosphere. Previously, we reported that microwave-discharge oxygen-plasma flow could attack polyacrylonitrile[14] and poly(ethylene terephthalate)[15] and enhance the decomposition of these polymers. This was due to the presence of oxygen atomic components in the plasma. In these cases, oxygen atomic species in the plasma glow enabled the polymer materials to rapidly react with the polymer and to introduce functional groups through the plasma surface treatment. In this work,

poly(vinyl chloride) (PVC) films were treated with oxygen plasma, which was produced by microwave discharge. The effect of the plasma treatment on the surface properties of the PVC films was examined.

EXPERIMENTAL

Materials

Oxygen (99.5%) was used as the carrier gas. PVC, with a degree of polymerization of 1030, was supplied by Nippon Zeon Co., Ltd., Tokyo, Japan. Other reagents were special-grade commercial types. PVC films, 100 μm thick, were prepared from a 20 wt % PVC/tetrahydrofuran solution at room temperature for a day and then were dried *in vacuo*.

Apparatus

The microwave-discharge system used for the plasma treatment of the PVC films is schematically shown in Figure 1. The chamber cell for the plasma treatment was composed of ϕ23-mm Pyrex glass 200 mm long. The glass tube was passed through a microwave cavity ($100 \times 300 \times 30$ mm^3), which was equipped with a Toshiba 2M172(YC)N magnetron (Tokyo, Japan) operated at 2.45 GHz and 500 W. Each film sample was placed in the chamber cell at the position in the cavity (shown by the dotted line) or 1 cm downstream from the cavity edge (shown by the solid line). The film was exposed to the discharge flow of oxygen at 1 Torr and at a 100 mL/min flow rate of the carrier gas. The pressure was controlled by a needle valve at the cavity

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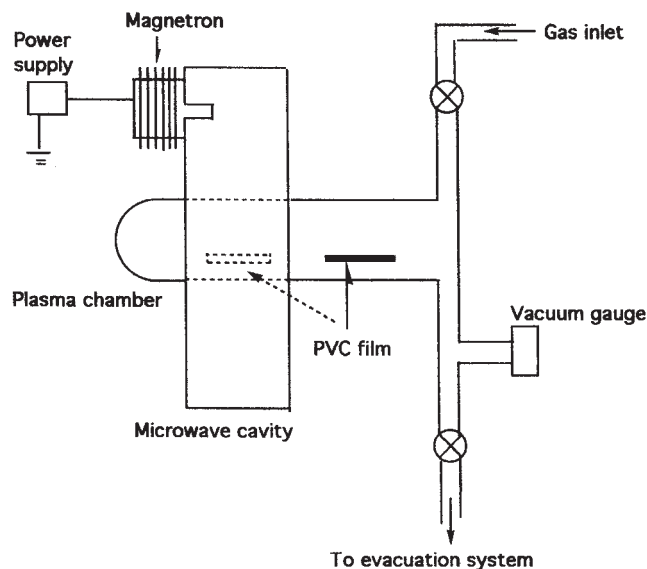
Figure 1 Schematic diagram of the equipment for the plasma treatment of PVC films.

and was measured with an MKS Barateon 122A vacuum gauge (MKS Japan, Tokyo, Japan). The flow rate of the feed was determined with a Kusano 1100 flow meter (Tokyo, Japan).

Measurements

The emission spectra of the plasma glow were measured as follows. The emission was focused by a silica optical fiber onto the entrance aperture of an MC-25NI spectrometer (30 cm and 300 groove/mm) (Tokyo, Japan) equipped with a Princeton Instruments IRY-512/R spectral multichannel analyzer (London, England). The diode-array detector, with 512 pixel elements, was connected to the multichannel analyzer. The time change of the emission spectral band was measured with an S2000 fiber-optic spectrometer (Ocean Optics, Inc., Dunedin, FL).

The morphology of the PVC film surface was observed with scanning electron microscopy (SEM; JMA-733, JEOL, Ltd., Tokyo, Japan). The sample surface for the SEM measurements was obtained via coating with gold with an SPM-112 spatter (Anelva, Tokyo, Japan).

The contact angle between the sample film and air or n-octane bubble was measured in water with a CA–A instrument (Kyowa Kagaku Co, Tokyo, Japan).

An NR-1100 (JEOL) laser Raman spectrometer equipped with an argon laser (514.5 nm and 100 mW) was used for the measurement of the Raman spectra of the films. Ultraviolet–visible/near-infrared (UV–vis/NIR) reflectant absorption spectra of the PVC films were measured with a V-570/PC system (Jasco, Tokyo, Japan). The sample compositions and functional groups of the polymer were also analyzed with X-ray

photoelectron spectroscopy (XPS; XP-HSIG, JEOL). The sample polymer powder was mounted on a sample stage with double-sided copper tape. For the measurements, an X-ray source (Mg Kα, 1253.6 eV) was used. The overview spectra were taken between 0 and 1000 eV with 1.0-eV steps, whereas the detailed spectrum of the peak of C1s was recorded with an energy step of 0.1 eV. For qualitative analysis, the curve fitting of XPS spectra was performed with a Gaussian distribution.
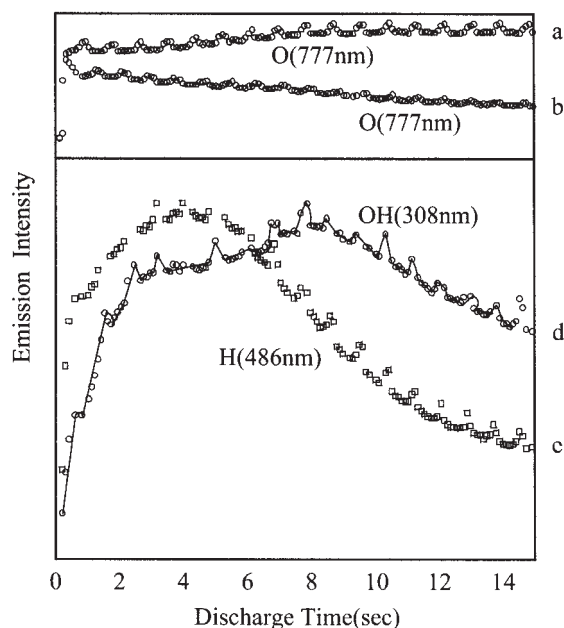
RESULTS AND DISCUSSION

Emission spectra of the oxygen-plasma glow

For the PVC film treatment by oxygen-plasma glow, the oxygen afterglow generated by the microwave discharge was greenish yellow. At the emission color
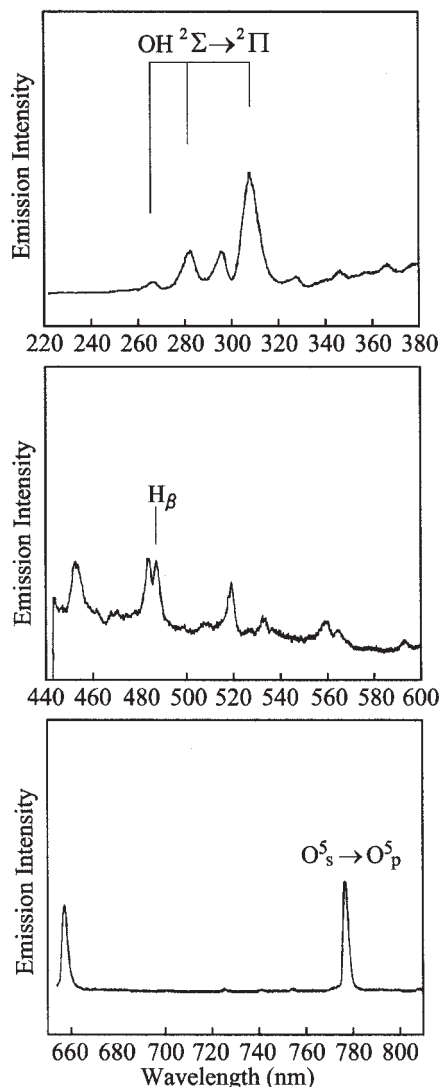

Figure 2 Emission spectra of oxygen plasma (a) in the absence of PVC and (b) in the presence of PVC at 1 Torr and a 100 mL/min flow rate.

Figure 3 Emission intensity of (a) the oxygen atomic line at 777 nm in the absence of PVC, (b) the oxygen atomic line in the presence of PVC, (c) the H_β atomic line at 486 nm, (d) the OH transition at 308 nm.

position, a typical spectrum of the oxygen atom showed an O^5S–O^5P atomic line[16,17] at 777 nm (Fig. 2). We confirmed that there were no bands in the visible region for the oxygen plasma. On the other hand, when the PVC film was placed in the chamber 1 cm downstream from the microwave-discharge-cavity edge, the band intensity of the O^5S–O^5P atomic line significantly decreased. Also, emission band peaks assigned to the OH ($^2\Sigma \rightarrow {}^2\Pi$) transitions[18,19] and H_β atomic line[16] were observed at 240–340 and 652 nm, respectively. Figure 3 shows time profiles of the emission intensity of the oxygen atomic line at 777 nm, the OH transition at 308 nm, and the H_β atomic line at 486 nm. The O_2 discharge began at time zero. In the absence of PVC, the 777-nm emission intensity of the oxygen atomic emission line immediately increased within a few seconds. Then, the emission intensity became constant. This indicated that the O_2 discharge was in the steady state in the range of the discharge times. In the presence of PVC, the oxygen emission intensity shown in Figure 3(b) similarly increased immediately, as shown in Figure 3(a). However, the emission intensity then gradually decreased with the discharge time. This suggested that the excited atomic oxygen species in the plasma was reduced by a reaction with PVC. The figure also shows time profiles of H_β and OH observed at 486 and 308 nm, respectively. The time profile was monitored at 486 nm for the H_β atomic line, as indicated in Figure 3(c). Thus, the emission intensity of the H_β line increased within about 4 s and then decreased slowly. However, for the OH band

at 308 nm [Fig. 3 (d)], the emission-band intensity had the maximum intensity at about 8 s and then subsequently showed a constant region of the emission intensity. These data suggested that the hydrogen species was generated by the PVC–plasma reaction, and the oxygen atom was consumed by the formation of OH species in the plasma. As we reported, for similar oxygen-plasma treatments of polyacrylonitrile[14] and poly(ethylene terephthalate),[15] the H_β atomic line was similarly observed. Therefore, the phenomenon commonly occurs in oxygen-plasma treatments of polymers even when the polymer species is changed. As d'Agostino[1] indicated, this may be due to two reactions:

$$RH + 2O^\bullet \rightarrow R^\bullet + H^\bullet + O_2$$

$$RH + O^\bullet \rightarrow R^\bullet + OH^\bullet$$
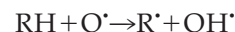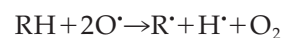
where R is an alkyl group.
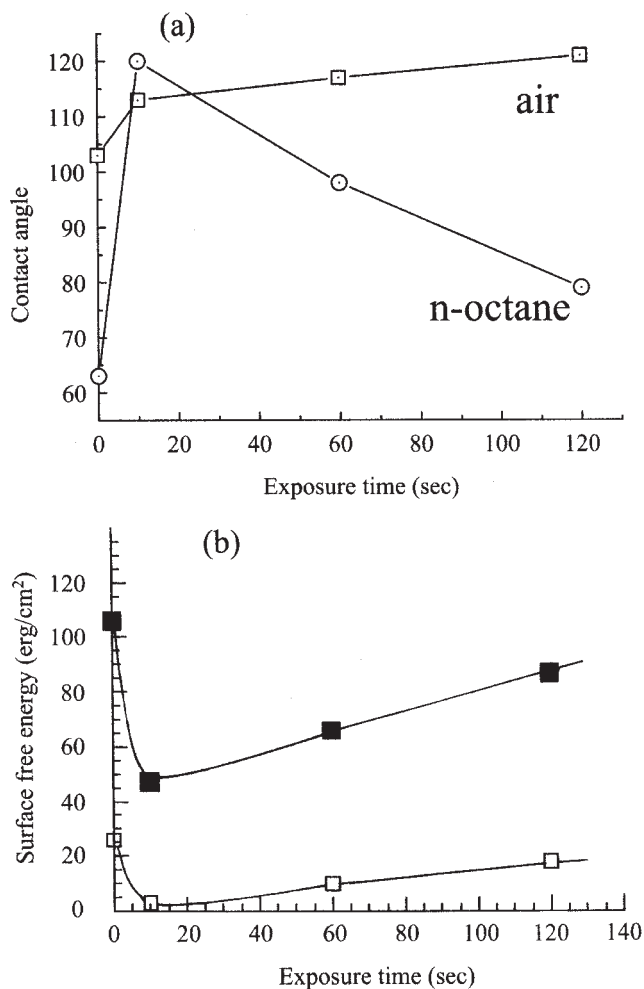
Figure 4 Figures 4 (a) θ_{air} and θ_{octane} in water and (b) γ_{SV} of PVC films treated with plasma afterglow at various exposure times: (■) γ_{SV}^d and (□) γ_{SV}^d.
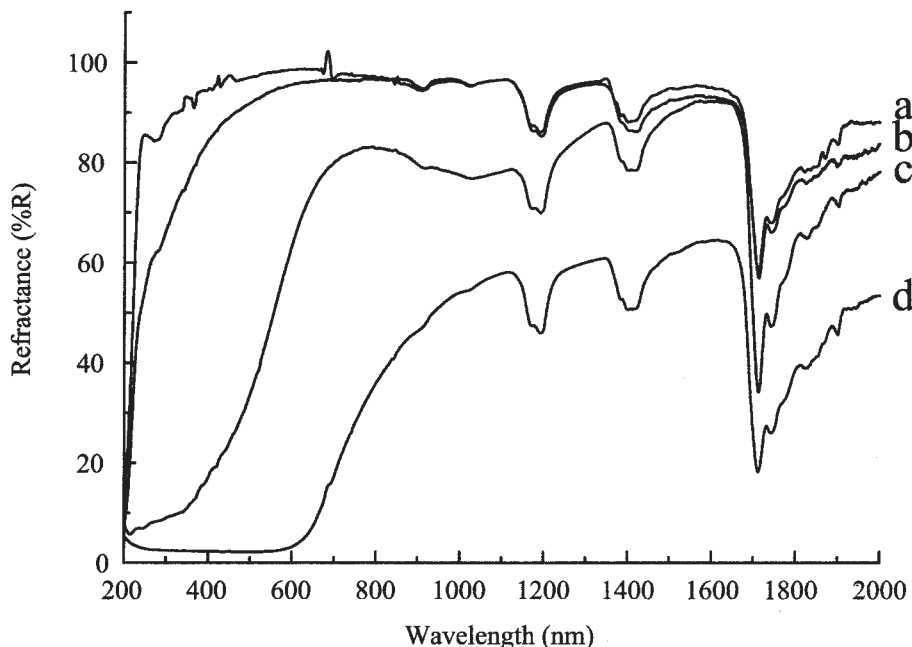
Figure 5 UV–vis/NIR spectra of PVC films treated with oxygen plasma at 1 cm downstream for various exposure times: (a) no treatment, (b) treatment for 4 s, (c) treatment for 30 s, and (d) treatment for 60 s.

Surface characteristics of PVC films treated with oxygen plasma

When the PVC film was exposed to the oxygen-plasma flow in the reaction chamber for 10 s, film changed to reddish brown. As the exposure increased, a carbonaceous film resulted. The Raman spectrum of the film was essentially identical to that of the carbon film;[20] typical broad peaks between 1100 and 1600 cm^{-1} for the carbon bonds of sp^2 and sp^3 were observed. This indicated that the carbonization of PVC rapidly occurred. Because of the significant shrinkage and carbonization of the PVC film, we treated it in the chamber downstream. When the film was placed 1 cm downstream from the cavity edge, the extent of film shrinkage and carbonization decreased. However, the shrinkage of the film in this position took place for an exposure time longer than about 300 s. When the film was set 3 cm downstream from the cavity edge, the reddish film was not obtained for longer than 300 s of exposure. Therefore, changes in the film properties affected by the exposure time of the plasma were studied 1 cm downstream.

To evaluate the surface properties of the treated films, we adopted the contact-angle method in water.[21] The contact angles of air (θ_{air}) and n-octane (θ_{octane}) for the films treated with plasmas are shown in Figure 4(a). The treatment of the PVC films by nitrogen plasma obviously increased the values of θ_{air} and θ_{octane}. The data suggested that the treated films were adverse to air and n-octane bubbles, being hydrophobic in nature, although the untreated PVC film had good wettability in air and in n-octane bubbles in water. The hydrophilicity on the film surface was improved by plasma treatment.[22] With the oxygen plasma, the values of θ_{air} and θ_{octane} increased. This indicated that the degree of hydrophobicity of the films was enhanced by plasma treatments longer than about 10 s.

To understand the contact-angle data in detail, we calculated the surface free energy (γ_{SV}) at the solid–vapor interface of the bubble with the method of Andrate et al.[21] Figure 4 shows plots of γ_{SV} of a treated film versus the exposure times for the plasma treatment. γ_{SV}^d and γ_{SV}^p are the dispersion and polar components of the surface tension, respectively. γ_{SV} is determined from the summation of the two components: $\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p$.

On the surface of a PVC film treated with the plasma afterglow of oxygen, γ_{SV} decreased. The treated surface had a larger dispersion component than a polar component: $\gamma_{SV}^d > \gamma_{SV}^p$. An increase in the dispersion term occurred with an increase in the treatment time. Because the change in γ_{SV}^d by plasma treatment was larger than that of γ_{SV}^p, the oxygen-plasma treatment clearly enhanced the degree of the hydrophobicity of the surface.

Figure 5 shows UV–vis/NIR spectra of PVC films exposed to oxygen afterglow at various times downstream. The PVC films showed broad absorption bands in the range of 400–600 nm. This strongly indicated that conjugated polyene bonds were formed. As reported by Maruyama and coworkers,[23,24] the polyene bonds
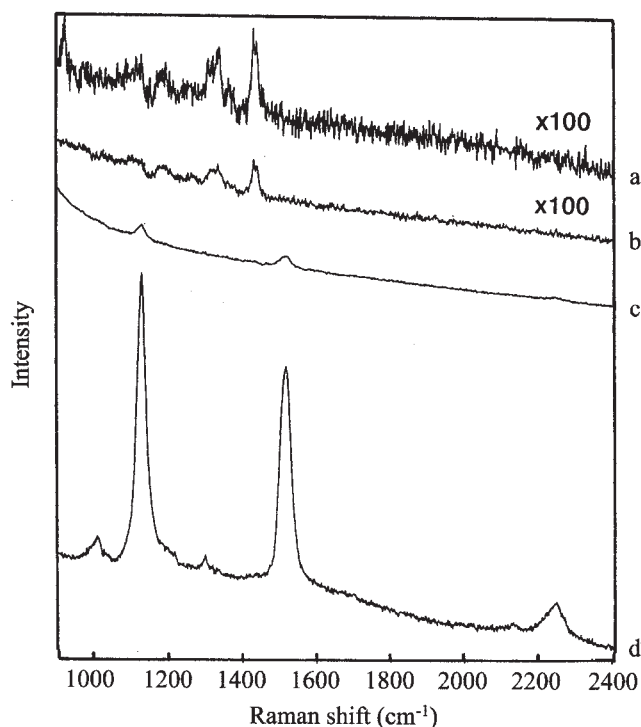
$$-\left(CH_2-CH_2\right)_n$$
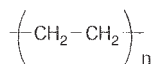
($n = 4$–12) showed absorption bonds in the range of 300–510 nm. Therefore, for the 30-s treatment in this work, the refractant spectrum indicated that similar numbers of

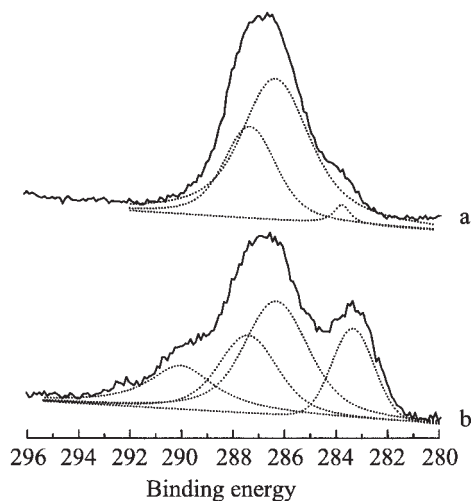$$-\left(\underset{H}{\overset{}{C}}=\underset{H}{\overset{}{C}}\right)_n-$$
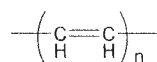
polymers were formed by the plasma treatment.

Polyene formation by plasma treatment

Figure 6(b–d) shows Raman spectra for PVC films treated for various exposure times in oxygen. Conjugated carbon bonds appeared at 900–2000 cm^{-1}.[25,26] Strong peaks at 1488 and 1121 cm^{-1} were assigned to the conjugated C=C stretching vibration[25] for a hybrid mode of CH in-plane bending and to C=C stretching for the C=C bond, respectively. The data showed that the Raman intensity of these peaks increased with an increase in the exposure time. In addition, for the 120-s treatment, a weak band at 2300 cm^{-1} was observed. This peak was assigned to a conjugated polyene bond.[27] From these Raman shifts for the approximately 1500-cm^{-1} band, the conjugated number n of polyene was esti-

Figure 7 XPS (C1s) profiles of (a) a PVC film and (b) the film after treatment with oxygen plasma for 120 s.

mated to be about 10 according to the method of Furukawa et al.[25] In the case of laser excitation for the Raman measurements, because the green beam (514.5 nm) of an argon laser was used, the excitation was restricted to only observations of the Raman band for the conjugated number $n = 10$.

Figure 7 shows XPS (C1s) profiles of PVC films with and without treatment by oxygen plasma for 120 min.
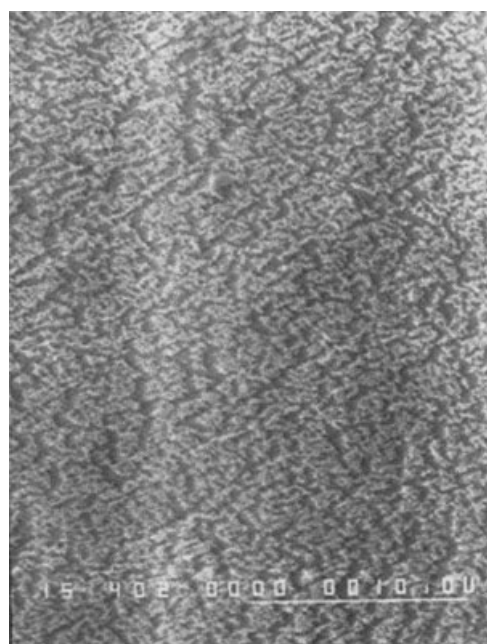
Figure 6 Raman spectra of PVC films treated with oxygen plasma: (a) no treatment, (b) treatment for 60 s, (c) treatment for 90 s, and (d) treatment for 120 s.

Figure 8 SEM micrograph of a PVC film treated with oxygen plasma for 120 s at 1 Torr (original magnification = 3000).

In the untreated PVC film, the deconvolution peaks had two components in C1s at 286 and 287 eV, which were assigned to C—C and C—Cl, respectively. In the profile of PVC treated with oxygen plasma, new peaks appeared at 284 and 290 eV and seemed likely to form C=C bonds and C=O groups on the treated surface. This fact indicated that the oxygen-plasma treatment formed C=C groups on the PVC surface, and this was supported by Raman spectroscopy.

An SEM photograph of a PVC film surface treated with oxygen was measured at a magnification of 3000×, as shown in Figure 8. The surface morphology of the PVC film after the oxygen-plasma treatment showed that the surface modification by the plasma was not homogeneous. This indicated the heterogeneous distribution of polymer formation on the PVC film because the etching process was proceeded by the layer treat-

ment. Therefore, the etched layers containing polymer layers had 1-μm patterns on the PVC surface.

There have been reports published on the preparation of conjugated polyene and polyne by photochemical methods.[24,28–30] For PVC, dehydrochlorination by photoirradiation is known to give rise to polyene segments in the PVC molecules. For example, polyene forms on a PVC film with photodegradation by UV light when a laser beam is exposed. The laser dehydrochlorination of a PVC film proceeds effectively with the irradiation of a laser beam. Because of the advantage of a laser for high spatial resolution, these processes are useful for pattern processing. On the other hand, as shown in Figure 8, a PVC film treated by oxygen plasma had an etching pattern on the surface.

In this work, the plasma treatment of PVC films caused both dechlorination and dehydrogenation as follows:
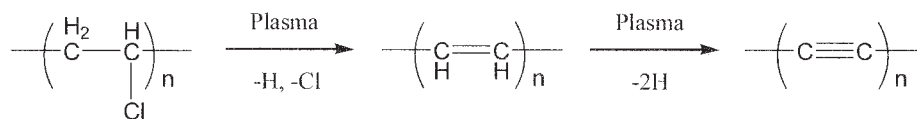
Thus, the microwave-plasma treatment showed interesting characteristics for polyene pattern processing on PVC films. However, various excited species in the plasma could result in further complicated plasma reactions with PVC films. Moreover, there are problems in the plasma treatment of PVC films with respect to pattern control. Also, heating a film by plasma glow results in a shrunk film and the carbonization of the film. However, we believe that this evidence of polyene formation is very interesting for surface functionality. Improvements in the apparatus and the treatment conditions are now being investigated to overcome these problems.

CONCLUSIONS

Conjugated polyene and polyne bonds on PVC films were rapidly formed by an oxygen-plasma treatment produced by microwave discharge. For the conjugated carbon bonds on PVC films, several analyses were applied.

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