Characterization and Properties of the Plasma Polymer Films prepared from Carbon Dioxide and 1,3-Butadiene

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We prepared plasma-polymerized thin films from a mixed gas of carbon dioxide and 1,3-butadiene. Their XPS and FT-IR spectra revealed that hydrophilic groups such as hydroxyl, carboxyl and carbonyl groups existed in the thin films. The content of the C-H carbons gradually decreased with increase in the plasma output power or the CO₂/butadiene flow rate ratio, while the amounts of carbonyl and carboxyl carbons increased correspondingly. In addition, coating of the plasma-polymerized CO₂/butadiene thin film on a polytetrafluoroethylene substrate was found to enhance the adhesion strength when the surface-modified substrate was bonded to a steel plate with an α -cyanoacrylate adhesive. These superior adhesion properties of the plasma-polymerized thin films formed on the substrates indicate that the oxygen-containing functional groups formed at the film surface play a major role in increasing the adhesion strength.

Keywords: plasma polymerization; carbon dioxide; 1,3-butadiene

1. Introduction

Plasma polymerization of organic monomers having various functional groups or plasma treatment of organic materials with various gases has been known to modify material surfaces by the introduction of various chemical structures and hence to be applicable to a wide variety of fields such as surface coating or surface treatment [1-7].

The thin films obtained by plasma polymerization of various organic monomers exhibit different performances, which can be attributed to the different functional groups of the monomers such as carboxyl, hydroxyl, amino or nitrile group. However, the functionality of plasma-polymerized thin films is attributed to the functional groups only at their surface and, the contents of which vary depending on the plasma polymerization conditions such as plasma output power, gas flow rate ratio or gas pressure [8-11]. Because the functional groups of monomers are easily destroyed or react under plasma conditions, the contents of functional groups in the thin films formed are in general smaller compared with those in the monomer.

On the other hand, plasma treatment of organic

materials with inorganic or organic gases such as fluorine, oxygen, nitrogen or tetrafluoromethane is a potentially attractive method for modifying the organic material surface by the introduction of hydrophilic or hydrophobic characteristics due to these gases. However, in general, plasma treatment also does severe damage to organic materials [12]. Besides, the duration of the performances attained by plasma treatment, especially, that of the hydrophilic characteristics is short [13].

We have already reported that plasma polymerization of 1,3-butadiene in the presence of oxygen [10] or nitrogen [11] for the introduction of various functional groups yielded thin films characterized by highly hydrophilic properties and their slow decay [10]. To our knowledge, few attempts have been made to use carbon dioxide as a monomer in plasma polymerization [14], except for plasma treatment by carbon dioxide or the conversion of methane in the presence of carbon dioxide within plasma [15]. In this article we report that plasma polymerization of a mixture gas consisting of carbon dioxide and 1,3-butadiene which produces hydrophilic thin films with high performances in

adhesion properties. Thus, the present paper discloses not only a new possibility of CO₂ as a reactant gas for plasma polymerization but also potential applications of the functionalized thin films produced.

2. Experimental

2.1. Reagents

1,3-Butadiene and carbon dioxide were purchased from Tokyo Kasei Kogyo Co., Ltd., Tokyo, and Suzuki Shokan Co., Ltd., Tokyo, respectively. These gases were used without further treatment.

2.2. Plasma polymerization

Two types of substrates were used for plasma polymer deposition. The glass substrate was micro slide glass, Shiromigaki No. 1 (76×26 mm², thickness; 0.8-1.0 mm, pre-cleaned), Matsunami Glass Ind., Ltd., was immersed in concentrated sulfuric acid for more than a day and then washed thoroughly with running tap water. It was sonicated in pure water containing a neutral detergent and then in pure water. Finally it was washed with methanol (GR grade) and dried. The polytetrafluoroethylene (PTFE) substrate (100×25×2.0 mm³), was washed with ethanol (GR grade) and dried.

Fig. 1 shows the schematic diagram of the setup of the apparatuses employed for the plasma polymerization. The plasma reactor tube was made of a Pyrex glass tube, 5 cm in diameter and 40 cm in length, which was fitted with a monomer inlet, a pressure gauge and an evacuation system. 1,3-Butadiene gas or a mixture of CO₂ and 1,3-butadiene was used as a reactant gas. The flow rate of each gas was controlled by the mass flow control system. The reaction system was evacuated to 38-73 Pa by using a rotary pump. Before the plasma polymerization the substrate was exposed to argon plasma for 1 min to eliminate the water and air adsorbed on the substrate surface. The substrate was either slide glass or PTFE, depending on the characterization methods. The plasma was maintained for 30 min at room temperature by an ac discharge at 1.2-6.0 kV using a neon sign transformer in combination with a commercial electric source (100 V, 50 Hz). The reaction system was kept below 40 °C by air cooling.

2.3. Spectroscopy

The Fourier transform infrared (FT-IR) spectra of plasma thin films were measured at room temperature by the KBr disk method, using a Nicolet FT-IR spectrometer, Model DX 50. The X-ray photoelectron spectroscopy (XPS) data were recorded at room temperature on a Shimadzu electron spectrometer, Model ESCA 750. The

Fig. 1 Plasma polymerization setup

Fig. 2 Sample setting in the shear stress test by the method of JIS K6850

spectra of the C_{1s} core level were resolved for component peaks using a Shimadzu ESCAPAC 760 data system.

2.4. Wettability

To estimate the relative wettability of a plasma-polymerized thin film, the contact angle of a water drop on the thin film deposited on a slide glass was measured at room temperature with use of a Kyowa contact angle meter, Model CA-D.

2.5. Crosscut test

The adhesive property of a plasma-polymerized thin film deposited on a slide glass was examined by the crosscut method according to JIS K5600 (JIS: Japanese Industrial Standards) [16]. In this method, an adhesive tape

(Cellophane tape No. 252, Sekisui Chemical Co., Ltd.) was used to peel off a plasma polymerized thin film, which had been crosscut to 100 squares (10×10 ; $1 \text{ mm} \times 1 \text{ mm}$ each), from the slide glass. The number of the crosscut pieces remained on the glass surface after the peeling was regarded as a measure of the adherence strength.

2.6. Adhesion test

Effect of the plasma polymer film on the adhesion strength was examined by the method of JIS K6850 [16]. To check this sample was set up as outlined in Fig. 2. A PTFE substrate on which a plasma-polymerized thin film had been coated was fixed to a steel plate with a glue having quick and strong bonding properties, i. e., α -cyanoacrylate adhesive (Three Bond 1741, Three Bond Co., Ltd., Tokyo) by an area of $10 \text{ mm} \times 25 \text{ mm}$. After 24 hours, the adhesion strength was measured with use of a Tensilon (Orientec Co., Ltd., Osaka).

3. Results and discussion

3.1. Identification and quantification of oxygenated carbons

Our previous study [10] on the plasma polymerization of butadiene- O_2 mixtures in an RF (13.56 MHz) plasma has disclosed that ablation and etching of the film formed became increasingly dominant on increasing the O_2 /butadiene flow rate ratio. Therefore, throughout this study, a commercial ac power source (100 V, 50 Hz) was amplified up to 6.0 kV with the help of a neon sign transformer to generate plasma. However, preliminary experiments of plasma polymerization by RF (13.56 MHz) discharge afforded almost the same results.

The plasma-polymerized thin film deposited on a slide glass was investigated by XPS and FT-IR spectroscopy to identify the functional groups formed. Fig. 3 depicts typical XPS spectra of the C_{1s} core level of the thin films obtained by plasma polymerization of butadiene in (a) the absence and (b) the presence of CO_2 at a CO_2 /butadiene flow rate ratio of 3.7, together with the resolved spectra shown by fine lines. A spectrum of the C_{1s} core level was resolved into four component spectra. In both cases, the largest peak at 285 eV is obviously due to the hydrogenated butadiene carbons to which no oxygen atoms are bonded. The peaks at 287, 288 and 289 eV can be assigned to ether or hydroxyl carbons, carbonyl carbons and carboxyl carbons, respectively. However, the content of the ether or carbonyl carbons appears to be extremely low, judging from its FT-IR spectrum (see Fig. 4) at $1070\text{--}1150$ or 1700 cm^{-1} , respectively. Although the peaks assignable to hydroxyl groups are also weak, we assign the XPS peak at 287 eV to hydroxyl carbons. The areas of the three peaks at 287, 288

Fig. 3 XPS spectra of the plasma-polymerized butadiene thin films prepared in (a) the absence and (b) the presence of CO_2 at a CO_2 /butadiene flow rate ratio of 3.7, together with the resolved peaks (shown by fine lines) for different types of carbons, i. e., hydrogenated carbons (285 eV), ether or hydroxy carbons (287 eV), carbonyl carbons (288 eV), and carboxyl carbons (289 eV).

Fig. 4 FT-IR spectra of the plasma-polymerized butadiene thin films prepared in (a) the absence and (b) the presence of CO_2 (Conditions: butadiene, 0.50 ml/min; CO_2 /butadiene flow rate ratio, 5.2; plasma discharge, 6.0 kV, 30 min)

and 289 eV for the thin film deposited in the presence of CO₂ (Fig. 3(b)) were much larger than the corresponding peaks for the thin film formed in the absence of CO₂ (Fig. 3(a)). Thus, the oxygenated carbons at the surface of the film prepared in the presence of CO₂ (Fig. 3(b)) must have been formed primarily by the reaction of the active species derived from butadiene with CO₂ in the gas mixture. The presence of the two peaks in the film obtained in the absence of CO₂, namely, without any oxygen source in the reactant gas (Fig. 3(a)), suggests that these oxygenated carbons must have been produced by the reaction of the active species derived from butadiene with the oxygen and/or water remaining in the reaction tube, and/or by the post-reaction in the air of the residual active species with oxygen, water and/or CO₂.

Fig. 4 represents the FT-IR spectra of the plasma-polymerized butadiene thin films in (a) the absence and (b) the presence of CO₂ at a CO₂/butadiene flow rate ratio of 5.2. The broad absorption band in the range of 1680 to 1715 cm⁻¹ of the film prepared in the presence of CO₂ (Fig. 4(b)) was stronger than the corresponding absorption band of the film prepared in the absence of CO₂ (Fig. 4(a)). The broad absorption band may therefore be attributed to carbonyl and carboxyl groups.

Thus, combining the IR and the XPS data allows us to conclude that the structure of the polybutadiene film deposited in the presence of CO₂ must have been partly destroyed and reacted to form new functional groups such as hydroxyl, carbonyl and carboxyl groups.

3.2. Effect of plasma polymerization conditions

Fig. 5 shows the variation of the XPS peak areas normalized by the total peak area of the four types of carbons on increasing the gas pressure, for the films produced at a constant CO₂/butadiene flow rate ratio of 3.7 and a plasma output power of 6.0 kV. Obviously, the contents of the four types of carbons at 285 eV (hydrogenated carbons), 287 eV (C-O), 288 (C=O) and 290 eV (COOH) varied only to a minor extent in the pressure range of 38 to 73 Pa.

Fig. 6 represents the variation of the XPS peak areas defined as above for the four different types of carbons in the films prepared at different plasma output powers in the range of 1.2 to 6.0 kV and a CO₂/butadiene flow rate ratio of 3.7. The peak area at 285 eV gradually decreased with increase in the plasma output power. On the other hand, the peak areas at 287 and 288 eV correspondingly increased, whereas that at 289 eV remained extremely low in this plasma output power range.

Similarly, Fig. 7 depicts the variation of the XPS peak

Fig. 5 Dependence of XPS peak areas of the plasma-polymerized thin film on the gas pressure (Conditions: butadiene flow rate, 0.50 ml/min; CO₂/butadiene flow rate ratio, 3.7; gas pressure, 43-63 Pa plasma discharge, 6.0 kV, 30 min)
○:hydrogenated carbons (285 eV), ●:ether or hydroxy carbons (287 eV), △:carbonyl carbons (288 eV), ▲:carboxyl carbons (289 eV).

Fig. 6 Dependence of XPS peak areas of the plasma-polymerized thin film on the plasma output power (Conditions: butadiene flow rate, 0.50 ml/min; CO₂/butadiene flow rate ratio: 3.7; gas pressure, 39-53 Pa; plasma discharge time, 30 min)
○:hydrogenated carbons (285 eV), ●:ether or hydroxy carbons (287 eV), △:carbonyl carbons (288 eV), ▲:carboxyl carbons (289 eV).

areas normalized as above for the films prepared at different CO₂/butadiene flow rate ratios, maintaining the plasma output power at a constant value of 6.0 kV at which the two types of functional groups were introduced in the plasma films to the greatest extent (Fig. 6). The peak areas of the oxygenated carbons at 287 and 288 eV gradually increased with increasing flow rate of CO₂ at a constant butadiene flow rate of 0.50 ml/min, whereas the peak area of the hydrogenated carbons at 285 eV decreased correspondingly.

The results in Figs. 5-7 strongly suggest that part of the C-H bonds of butadiene were converted to the

Fig. 7 Dependence of XPS peak areas on the CO₂/butadiene flow rate ratio (Conditions: butadiene flow rate, 0.50 ml/min; gas pressure, 43-63 Pa; plasma discharge, 6.0 kV, 30 min)
 ○:hydrogenated carbons (285 eV), ●:ether or hydroxy carbons (287 eV), △:carbonyl carbons (288 eV), ▲:carboxyl carbons (289 eV).

oxygenated carbon groups. The leveling off of the contents of the two types of functional groups in the film with increasing variables in the abscissas could be due to increasing destruction of the functional groups with plasma and/or to increasing degree of cross-linking in the film, which would make further introduction of the functional groups increasingly difficult.

3.3. Properties of plasma-polymerized films

The wettability and adhesion property of the plasma-polymerized thin films prepared at varied CO₂/butadiene flow rate ratios were investigated to unravel their performances due to the functional groups introduced.

3.3.1. Wettability

The wettability of the plasma-polymerized CO₂/butadiene thin film was estimated by the contact angle of a water drop on the film deposited on a slide glass. As summarized in Table 1, the contact angle decreases with increasing CO₂/butadiene flow rate ratio at a constant butadiene flow rate, reflecting increasing hydrophilicity of the film surface owing to the oxygenated carbon groups introduced by the plasma polymerization (Figs. 4-7).

3.3.2. Adherence to glass substrate

The adhesion property of a plasma-polymerized thin film to a slide glass was determined by the method of JIS K5400, i. e., the crosscut method [11]. Table also shows that increasing the CO₂/butadiene flow rate ratio in the reactant gas resulted in the increase of the adhesion strength of the plasma polymerized thin film formed on a slide glass.

Remarkably, no crosscut pieces came off out of 100 square cut films, each of which has a square area of 1 × 1 mm², when the film prepared at a CO₂/butadiene flow rate ratio of 0.8 or higher was tested.

Thus, increasing the amount of CO₂ in the gas mixture for plasma polymerization increased not only the hydrophilicity but also the adherence strength of the resulting thin film to the glass substrate, most probably owing to the increasing content of the hydrophilic groups including hydroxyl, carbonyl and carboxyl groups at the film surface.

3.3.3. Adhesion strength

To further evaluate the performance of the thin films obtained the adhesion strength was measured by the JIS K6850 method [11]. The sample was set up as illustrated in Fig. 2; a PTFE plate on which a plasma-polymerized thin film had been deposited was bonded to a steel plate with an α -cyanoacrylate adhesive (For details, see Experimental.) . Figure 8 presents the adhesion strength data obtained with plasma polymer films prepared from CO₂ and butadiene at different CO₂/butadiene flow rate ratios in comparison with those [8] obtained with the corresponding films prepared from O₂ and butadiene. Without using any plasma-polymerized film, the adhesion strength was as low as 10.1 kg/cm². The adhesion strength increased linearly with increase in the CO₂/butadiene flow rate ratio.

However, with the plasma polymer films prepared from O₂ and butadiene, the adhesion strength increased with addition of O₂ but decreased on further addition of O₂, as reported in our previous paper [8]. It is likely that in the plasma polymerization of the O₂-butadiene mixture, increasing the O₂/butadiene flow rate ratio results in an

Table1. The wettability and adhesion test of plasma polymerized CO₂-butadiene thin films

CO ₂ / butadiene ^a ratio (v/v)	0.0	0.4	0.8	2.2	3.8	5.2	7.4
Contact angle (degree)	75	75	76	60	66	44	24
Cross cut (X/100) ^b	88	45	100	100	100	100	100

^a Conditions: 1,3-butadiene, 0.5 ml/min; plasma polymerization, 6.0 kV, 30 min.

^b Number of the pieces remained on the substrate after peeling.

Fig. 8 Effect of CO₂ or O₂ / butadiene flow ratio on the adhesion strength between PTFE substrate coated by plasma polymerized CO₂ or O₂-butadiene film and steel plate.

increasing destruction of the functional groups once formed or an increasing ablation and etching of the plasma film. The adhesion properties of the plasma polymers from the two systems are in harmony with our previous studies on plasma polymers from butadiene and nitrogen [9].

However, it should be noted that the IR and XPS spectroscopic studies [8] have shown that, although the two types of plasma polymers have both carbonyl and carboxyl groups, the plasma polymers from the O₂/butadiene system have more carboxyl groups than the plasma polymers from the CO₂/butadiene system. A further investigation is needed to confirm this point.

4. Conclusions

Although the mechanisms of plasma polymerization are complicated and have not been established in detail, plasma polymerization process permits us to use various kinds of monomers and their mixtures for film deposition. In the present study, attempts were made for the first time to introduce hydrophilic functional groups into hydrophobic polybutadiene by plasma polymerization of a mixture of CO₂ and 1,3-butadiene. The XPS and FT-IR spectroscopic studies on the films produced from butadiene alone and a mixture of CO₂ and butadiene revealed that increase in the plasma output power or CO₂/butadiene flow rate ratio gradually increased the contents of the oxygenated carbons such as hydroxyl, carbonyl and carboxyl groups in the films produced. Their wettability to a water drop and adherence to a glass substrate were enhanced correspondingly. It was revealed that the plasma polymers from the CO₂/butadiene

system was effective for increasing the adhesion between a plasma polymer-coated PTFE plate and a steel plate.

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