ThreeBond TECHNICAL NEWS

Three Bond Technical News
Issued Jul. 10, 1989

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Surface Modification of Polymers Applying Plasma

1. Introduction

Recently, since providing features such as adhesive property, abrasion resistance, electrostatic property, anti-fog property, water repellency, and biocompatibility with the surface of polymer materials is requested strongly, much research concerning the method of surface modification of polymers has been done. For example, as surface modification of polyolefin polymer, the methods in Table 1 are known.$^{1)}$

Merits of plasma treatment method are as follows:

1) It is just surface modification, which does not influence the bulk characteristics of polymers.

2) Since it uses low-temperature plasma, it is suitable for modification of polymers, which have low heat resistance compared with metal.

3) Surfaces with unprecedented new structure and characteristics can be created for the first time.

4) Since reaction system is the driving process, it is clean and energy conservation.

However, there are problems such as that it is treated in vacuum normally and reaction control is difficult.

Plasma treatments include plasma surface modification using non-polymerizable gas (such as Ar, N_2, and O_2) and plasma polymerization, which conduct coating treatment on the surface of the material using organic monomer (organic metal monomer) to make a thin polymer film. Both methods are compared in Table 2.$^{2)}$

The effects of plasma treatment include forming a surface crosslinked layer using non-responsive gas such as He or Ar, introducing functional groups using responsive gas such as N_2 or O_2, and surface etching using Ar or O_2 gas.

As applications for plasma surface treatment, there are many applications related to hydrophilicity and hydrophobicity such as improving biocompatibility, adhesion property, and dye-affinity and providing water repellency using fluorine gas by the improvement in hydrophilicity (Table 3).

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Table 1. Surface modification method of polyolefin resin

Class	Treatment Method	Practical Examples	Advantages	Disadvantages
Wet process	Dip treatment using oxidative compounds represented by chromic acid.	Potassium dichromate 75 units Concentrated sulfuric acid 500 units Water 200 units 70°C dip 15 seconds	Shape does not matter Uniform treatment is possible	Persistent chemical compounds Environmental pollution
	Chlorinated PO, primer treatment of such as copolymer of ethylene and vinyl acetate	Commercially available from several companies	Simple and low cost	Bad heat resistance of adhesion Bad solvent resistance of adhesion
	Roughening surface dip treatment using halogenated hydrocarbon solvent	Ethylene trichloride 70°C dip 30 seconds	Simple and low cost	Effects are small
	Graft reaction and copolymerization reaction treatment	Introduce polar compounds chemically into PO chains	Great effects	High cost
Dry process	Corona discharge process	Corona discharge under air or oxygen at normal pressure	Great effects with burst flame gas treatment	Difficult with complex shapes
	Ozone treatment	Used concomitantly with UV irradiation (250nm)	Great effects	Pollution of environment due to ozone
	Plasma discharge treatment	Plasma discharge in vacuum	Great effects	Difficult for large objects Continuous production is difficult
	Radical activation processing using UV and electron beam	UV (340nm) or gamma ray treatment	Great effects with EPDM, etc.	Electron beam irradiation requires special equipment
	Oxidation treatment using flame	Several seconds with oxidizing flame at around 1500°C	Simple and low cost	Uniform treatment is difficult

Table 2. Comparison of plasma polymerization and plasma surface treatment in surface modification of polymers

	Plasma polymerization	Plasma surface treatment
Surface property		
Degree of modification	○	△
Adherability at interface	△	○
Stability		
Water and solvent resistances	○	○
Acid and alkali resistances	○ – △	△
Durability	△	○ – △
Control of treatment		
Control of treatment condition	△	○
Contamination inside reaction system	×	○

Table 3. Improvement of adhesive properties of polymeric materials by plasma treatment [2] Unit (p)

Material	Untreated	He plasma treatment		O_2 plasma treatment		N_2 plasma treatment
	372	30s	300min	30s	30min	
Low density polyethylene	372	1250	1324	1446	1446	1401
High density polyethylene	315	924	3125	1984	2436	3500
Polypropylene	370	450	200	1870	3080	633
Polystyrene	566	–	4015	–	3118	–
Nylon 6	846	1220	3956	1624	3490	–
Polyethyleneterephthalate	530	–	1660	–	1212	–
Polyvinyl fluoride	278	1290	1200	1370	1280	–
Cellulose acetate butyrate	655	1250	2516	1126	1380	–
Polycarbonate	410	660	840	800	928	–
Polyoxymethylene	118	186	236	–	258	–

Plasma treatment conditions: 13.56MHz, 50W, 0.3mmHg; Gas flow rate: 20ml/min

2. Surface Modification of Polymers by Plasma Polymerization Treatment

With plasma surface modification, since chemical structure of the surface cannot be changed drastically due to restricted processed gas, it is not expected to get modified surface with absolutely different chemical and physical properties from the bulk one.

In the meantime, the polymerization process of organic compounds in low temperature plasma is different from conventional chemical polymerization method. Any organic compounds (for example, ethane or benzene) can be candidates for polymerization monomers on principle. Due to this characteristic and merit that the obtained organic thin films possess highly crosslinked structures, application deployment of functional materials utilizing characteristics of polymerized films is expected.

In addition, plasma polymerization of organic compounds is utilized in such as preparation of uniform organic thin films without pinholes and surface modification of polymers. Active research of functional organic thin films with electric properties for sensors and semiconductors, etc. is carried out as well.[3-5)]

In this issue, we describe mainly our research examples regarding surface processing method of polymer compounds.

3. Plasma Polymerization of Butadiene/Oxygen Mixed Gas

Plasma polymerization is a severe reaction with the electronic temperature in the reaction container as high as tens of thousands Centigrade (Figure 1). Since functional groups in polymerization monomers are destroyed, decomposed, and cut in plasma, it is quite difficult to introduce functional groups in thin films, which develop functionality.

However, by introducing responsive gasses in addition to gasses of organic compounds, introduction of several functional groups into thin films has become available. There are some reports recently. [6-9)]

We have performed plasma polymerization of butadiene under oxygen (O_2) gas, and investigated the structure and functionality of the generated thin films in detail. [10)]

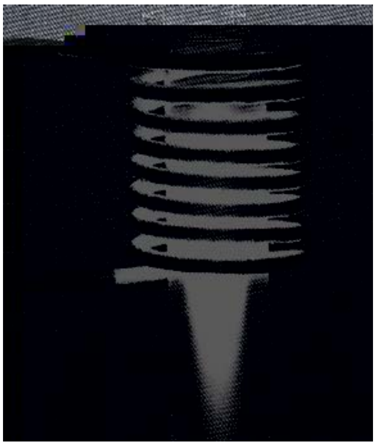
What is Plasma?

We often hear the term plasma recently. It generally suggests “high temperature plasma” such as in nuclear fusion or plasma spray coating. The plasma used for surface modification of polymers and used as energy source to make thin films is mainly the “low temperature plasma” generated by glow discharge.

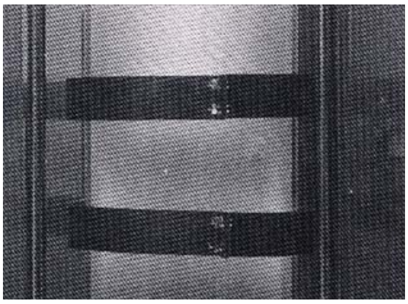
Plasma is often observed in our daily lives as well. For example, lightning caused by discharge in air and gasses in fluorescent lights and neon signs are in the state of plasma. In addition, the space is in the plasma state.

To describe what is plasma like, it is electrically neutral ionized gas as mentioned as the forth state of substance following the solid, liquid, and gas. There are active species such as electrons, ions, radicals, and photons, which are origins to polymerize organic monomers. It is the so-called very active gas. It is suggested that a life also has been created from amino acids generated by the discharge in primitive atmosphere.

To generate plasma, a glass tube with electrodes on both ends is used. When the pressure in the system is reduced below 10^{-1} to 1 Torr using a vacuum pump and the voltage of several hundred volts is applied to the electrodes, tangerine ray is generated. For the power supply, besides DC, high frequency or microwave power supplies are used.



High temperature plasma



Low temperature plasma

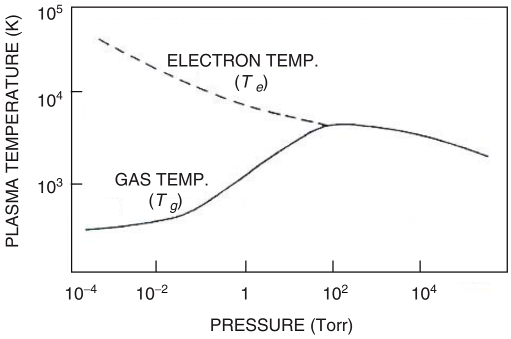


Figure 1. Gas pressure and plasma temperature

3-1. Reaction Reagents

For 1,3-butadiene (Tokyo Kasei Kogyo Co., Ltd.), oxygen, argon, and carbonic acid gas (Suzuki Shokan Co., Ltd.), products on the market have been used as is.

3-2. Plasma Polymerization Apparatus and Film Formation Method

For plasma polymerization apparatus[11)], cylinder type reaction tube made from pyrex glass with 50mm diameter illustrated in Figure 2 was used. Plasma was generated by amplifying commercial power using neon sign transformer. With the plasma output of 6KV, the reaction tube was decompressed by an oil-sealed rotary pump, and 1,3-butadiene gas and O_2 gas was introduced to the reaction tube. The flow was controlled by the mass flow controller to the designated mixture ratio. With the total gas flow of 0.9 to 2.2 sccm, the vacuum degree in the system was controlled within the range from 0.2 to 0.5 Torr. To prevent the heat due to plasma, wind cooling was conducted to keep the temperature in the system below 40°C.

For substrates, glass slides, PTFE (Teflon) or KBr plates were used according to the purpose. After pre-rinsing, argon etching was conducted to remove gas and contaminants adsorbed on the surface of the substrates.

The same experiment has been conducted using a high frequency power (13.56MHz) as a source of plasma; however, in this case, as the increase in mixture ratio of O_2, etching has become predominant. Because of this difficulty in film production, plasma was generated by commercial power in this research.

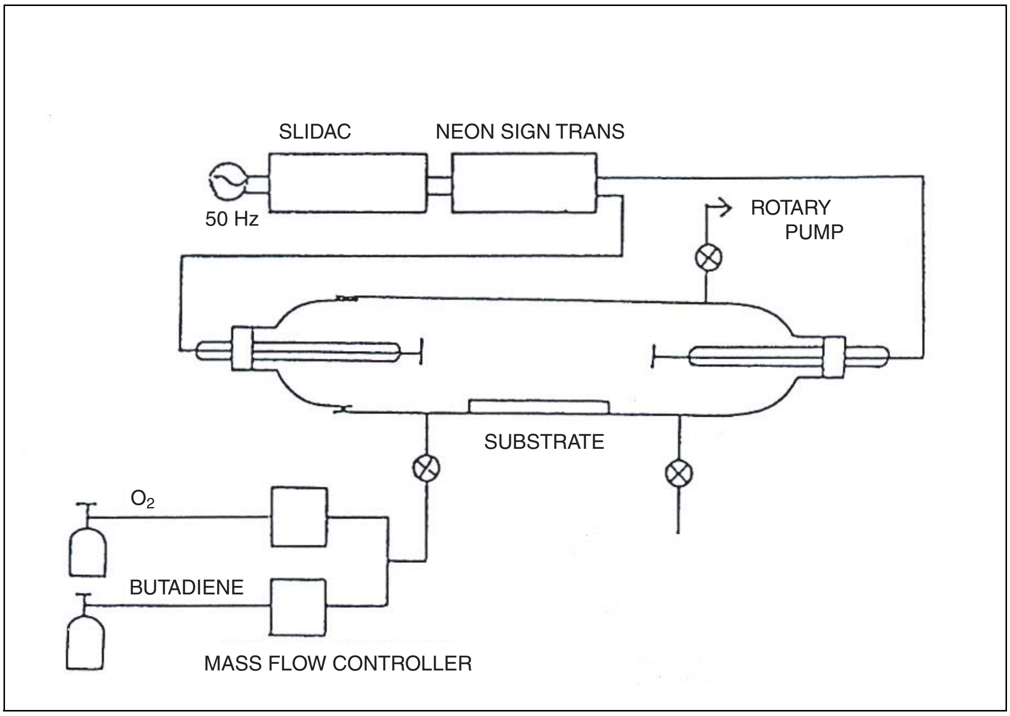


Figure 2. Plasma apparatus

3-3. Evaluation Method of Generated Thin Films

1) Structure of the generated thin films were examined using the following analytical instruments. For X-ray photoelectron spectrum (XPS), X- ray photoelectron spectroscopy ESCA750 of Shimadzu Corp. and for infrared spectrometer (FT – IR), DX50 of Nicolet Corp were used, respectively.

2) Quantitative method of functional groups by derivatization method: butadiene-O_2 plasma polymer films deposited on glass substrates with several mixture ratio were dipped in the mixed solution of trifluoroacetic anhydride, benzene, and pyridine for reaction for 1 and a half hours. After the reaction, the substrates were rinsed with benzene and rinsed with ethyl ether in the Soxhlet extractor for 12 hours. After drying, quantitative method was conducted by XPS. [12)]

3) A drop of water was dropped on the thin films generated and the contact angles were measured using a contact angle meter CA – D made by Kyowa Kagaku Co., Ltd.

4) Adhesion of the deposited thin films on the glass substrate to the substrate was evaluated by the cross cut test complying with JIS (Japanese Industrial Standard) K 5400. The cross cut test is the test to examine adhesion of films. By cutting generated thin films 11 times crosswise using a cutter with the interval of 1mm, 100 squares are prepared. After pressure joining adhesive tapes on them, they are peeled off. Then the number of squares remained are counted.

5) For adhesion test, shearing properties were measured complying with JIS (Japanese Industrial Standard) K 6850. For adhesives, instant adhesive (ThreeBond 1741) was used. A steel (SPCC – SD) plate was joined to the PTFE substrate, which was treated by plasma polymerization, as illustrated in Figure 3. After 24 hours of curing, shearing properties were measured by the tensile tester (TENSILON).

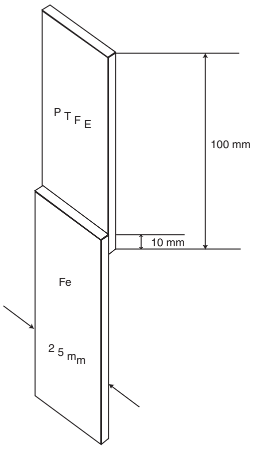
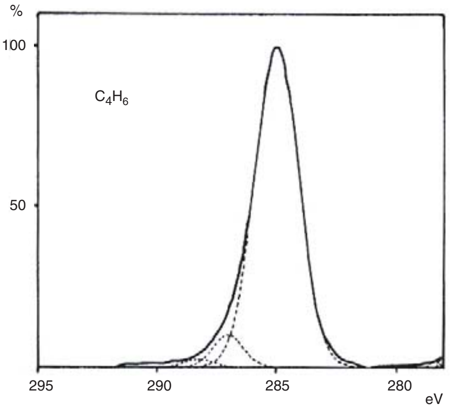


Figure 3. Adhesion test by JIS (Japanese Industrial Standard) K6850 method

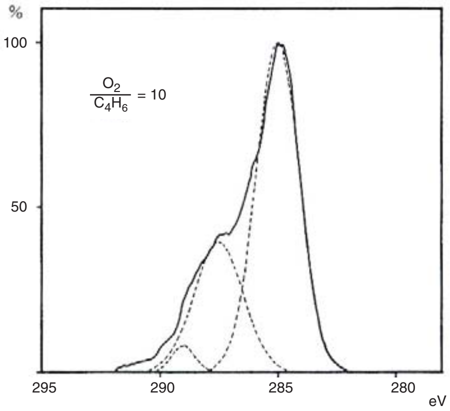
3-4. Results and Discussion

(1) Chemical Structure of Butadiene-O_2 Plasma Thin Films

Figure 4 shows the C_{1s} peaks of XPS spectra of single butadiene plasma thin film (a) and butadiene-O_2 plasma thin film (b) with 1/10 mixture ratio of butadiene/O_2 gas. The high peaks at 285eV of carbon originated from hydrocarbon are observed with both thin films. However, in addition, the significant peaks of carbonyl group carbon, ether carbon (287eV), and carboxyl group carbon (289eV) are observed with the plasma polymer film under O_2 gas introduction, indicating that functional groups are generated in the thin film due to the reaction of O_2. The peaks (287eV and 289eV), which include oxygen, observed slightly with the single butadiene thin film are assumed to be originated from the products generated from small amount of remaining oxygen in the reaction system or the products generated by the reaction with oxygen in the air after depositing the thin film.



(a) without O_2



(b) with O_2

Figure 4. XPS spectra of butadiene-O_2 thin films

Figure 5 (a) shows IR spectra of butadiene-O_2 plasma thin film. The existence of carbonyl group ($1715cm^{-1}$) and carboxyl group (1680 to $1710cm^{-1}$) in the structure of the generated thin film is recognized. The absorption of hydroxyl group of 3200 to $3500cm^{-1}$, which emerges with surface modification by oxygen plasma treatment of polymeric material, was scarcely observed.

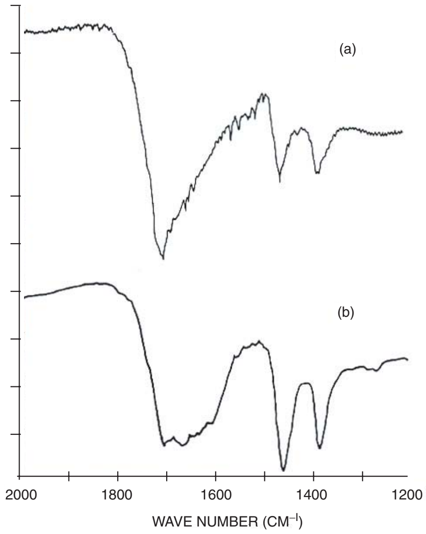


Figure 5. FT-IR spectra of the plasma polymerized thin films (a), butadiene-O_2 thin film; (b), butadiene-CO_2 thin film

As quantitative method for this carboxyl group, derivatization method was adopted. Table 4 shows the results. The derivatization method is the method to estimate the quantity of carboxyl group by quantifying F or Br from XPS spectra after the reaction of functional groups in the thin film with chemical compounds, which contain F or Br element. In this section, the reaction was conducted with generated thin films and trifluoroacetic anhydride. In this case, although the functional groups will react with not only carboxyl groups but also hydroxyl groups, since it is clear that there are few hydroxyl groups in the thin films from the results of IR spectra, it is considered that values in Table 4 are almost contents of carboxyl groups.

Table 4. Amount of carboxyl group in butadiene-O_2 thin film determined by derivatization method.[a)]

O_2/butadiene ratio	Carboxyl group[b)]
1.0	4.0
5.0	5.8

a) Treated by $(CF_3CO)_2O$

b) The atomic ratio of the carbon atoms of the carboxyl group to total carbon atoms in the film.

(2) Wetting Characteristic of Butadiene-O_2 Thin Films

We have evaluated hydrophilic properties of surface of butadiene-O_2 plasma thin films by measuring contact angles with water. As shown in Table 5, as the flow rate of O_2 gas increases, the contact angle of generated thin films with water decreases, where the flow rate of butadiene is constant. It means improvement in wettability due to the increase in hydrophilic groups in thin films. It coincides with the fact that as O_2 flow increases, the content of functional groups, which include oxygen, such as carbonyl group and carboxyl group in the films increases.

In addition, regarding adhesion between plasma thin films and glass substrates, peeling is observed in case of single butadiene plasma thin films, which means adhesion is not so good. However, for butadiene-O_2 plasma thin films, peeling has never been observed, which means introducing small amount of O_2 gas into plasma improves adhesion.

(3) Adhesive Properties and Sustainability of Butadiene-O_2 Thin Films

As described above, since butadiene-O_2 thin films can change mixture ratio of butadiene/O_2 gas, hydrophilic properties of the film surface can be easily controlled. Therefore, we have examined the application as the surface modification of polymers by depositing butadiene-O_2 thin films on polymeric materials.

Although PTFE (Teflon) is the material with low adhesive property, we have examined adhesive properties with different materials by depositing butadiene-O_2 thin films on PTFE under several conditions. Table 6 shows the results. Compared with the untreated blank sample, the adhesion force of all the samples with plasma polymerization treatment were improved. Furthermore, the results show quite excellent values compared with the case of primer treatment, which is used for improvement of PTFE adhesion force.

As surface modification of polymers, above-mentioned plasma treatment using Ar or O_2 gas is conducted; however, as time passes after the plasma treatment, it is known that the wetting properties of the surface is weakened.

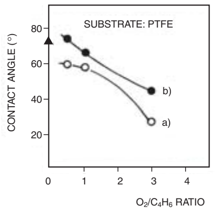


Figure 6. Time dependences of contact angle of the plasma polymerized butadiene-O_2 thin film. a), immediately after plasma polymerization; b), after 2 months.

It is because as time passes, they are taken into the polymeric material due to the rotation of hydrophilic groups of the surface inside molecules. Compared with this, since highly crosslinked polymerized films prevent the movement of hydrophilic groups generated on the surface into the bulk objects in the case of plasma polymerized thin films, sustainability is expected. (Figure 6).

Although in case that the hydrophilic property of the thin film surface is low, it becomes almost the same to the untreated one after 2 months or so, in case of thin films with high hydrophilic property of the surface, it is almost maintained even after 2 months. 9)

As mentioned above, by plasma polymerization of butadiene mixed with oxygen gas, it has become clear that functional groups such as carbonyl group and carboxyl group will be introduced into the thin films.

For butadiene-O_2 plasma polymerized thin films, hydrophilic property of the surface of the thin films can be easily controlled by changing the mixture ratio of butadiene/O_2 gas. Moreover, the functionality of these butadiene-O_2 plasma polymerized thin films is sustained compared with the ones with argon or oxygen plasma treatment.

Table 5. Effects of oxygen gas on the wettability and adhesion properties of butadiene-O_2 thin film[a)]

O_2/butadiene ratio	Contact angle (°)	Cross cut (X/100)
0	75	88
0.5	69	100
1.0	72	100
2.0	63	100
3.0	47	100
5.0	33	100
7.0	7	100
10	5	100

a) The wettability of the thin film was estimated by the contact angle with water. The adhesion property of the thin film with glass substrate was measured by cross cut test.

Table 6. The effect of coating by butadiene-O_2 film on the shear stress of PTFE joined at a steel by adhesives [a)]

O_2 flow rate (scom)	Shear strength (kgf/cm^2)
0.5	19.7
1.0	20.1
2.0	17.8
Untreated PTFE	10.1
Primer treatment	14.9

a) Butadiene: 1.0sccm

4. Plasma Polymerization of Mixed gas of Butadiene/Carbon Dioxide Gas

Although the number of carboxyl groups is drastically reduced when carbonic acid derivatives are polymerized in plasma, the reduction in carboxyl group is suppressed by introducing CO_2. In this section we will examine organic thin films, which are plasma polymerized organic compounds (1,3-butadiene) without carboxyl group under CO_2 existence.

Organic thin films were deposited by the same polymerizer as the above-mentioned one butadiene-O_2 thin films. From the results of the XPS spectra of the obtained thin films, the structure of carbonyl group carbon, ether carbon (287eV), and carboxyl group carbon (289eV), all of which cannot be obtained by plasma polymerization of single 1,3-butadiene, was recognized (Figure 7). The changes of the area of the 285eV peak of hydrocarbon carbon and the 287eV peak of carbonyl group carbon of the thin films deposited with various mixture ratio of butadiene and CO_2 and butadiene and O_2 gas are shown in Figure 8. It is recognized that as flow of CO_2 and O_2 gasses increase, the peak area ratio of carbons combined with oxygen atoms increases.

Furthermore, the existence of carbonyl groups and carboxyl groups has been proved by the results of IR spectrum shown in Figure 5 (b). It is recognized that the butadiene-O_2 thin films are with less carbonyl groups and abundant with carboxyl groups.

Although the content of carbonyl group and carboxyl group also increases, as CO_2 ratio in the mixed gas increase, it becomes almost constant at the CO_2/butadiene ratio of 1.1/0.5 or more. Moreover, wettability with water and adhesion to substrates improved as CO_2 ratio increases. It is assumed because of the increase in the number of hydrophilic groups (Table 7). [13)]

In addition, although the adhesive properties with different material (PTFE/Fe) is poor compared with butadiene-O_2 thin films, almost the equal level values to that of the one with primer treatment have been obtained (Table 8).

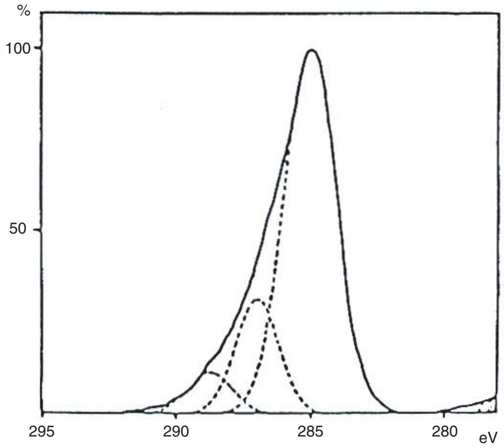


Figure 7. XPS spectra of butadiene-CO_2 thin film

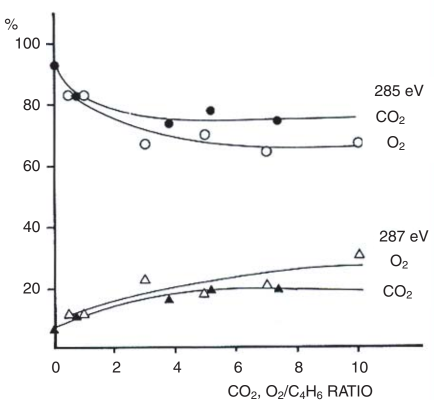


Figure 8. The variation of oxygen content in the thin films depending upon the difference of the gas mixture ratio at butadiene-CO_2 system or butadiene-O_2 system

Table 7. Effects of oxygen gas on the wettability and adhesion properties of butadiene-O_2 thin film

CO_2/butadiene ratio	Contact angle (°)	Cross cut (X/100)
0	75	88
0.4	75	45
0.8	76	100
2.2	60	100
3.8	66	100
5.4	44	100
7.2	24	100

Table 8. The effect of coating by butadiene-CO_2 film on the shear stress of PTFE joined at a steel by adhesives [a)]

CO_2 flow rate (sccm)	Shear strength (kgf/cm^2)
0.5	11.0
1.1	14.7
1.9	15.2
Untreated PTFE	10.1
Primer treatment	14.9

a) Butadiene: 0.5sccm

5. Plasma Polymerization of Butadiene/Nitrogen Mixed Gas

Butadiene/N_2 thin films have been deposited in the same way with the other mixed system. Figure 9 shows the results of FT-IR spectrum of the obtained thin films. The inclusion of amino groups (3300cm^{-1}) and nitrile groups (2200cm^{-1}) in the structure of the generated thin film was recognized. Table 9 shows the contents of nitrogen and oxygen estimated from the XPS spectra. As N_2 mixture ratio increases, the content of nitrogen also increases. Table 10 shows the results of adhesion to the substrates and the adhesive properties to a steel, which were measured by coating on PE. More than 5 times of strength was obtained compared with the case of untreated one. [14)]

As mentioned above, composite films of organic compounds/responsive gas have been examined; however, from the viewpoint of adhesion, plasma treatment using Ar or O_2 gas and etc. is convenient and practical because of high bonding strength.

However, since there are merits such as controllability and sustainability of hydrophilic and hydrophobic properties by changing the combination and mixture ratio of raw material gasses are expected with plasma polymerization, more research should be done.

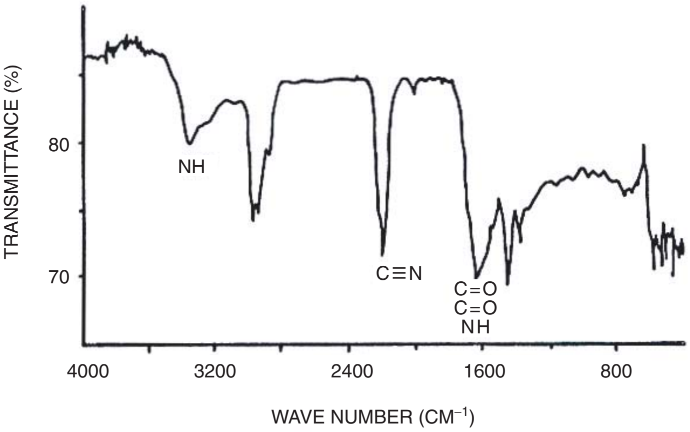


Figure 9. FT-IR spectrum of the plasma polymerized butadiene-N_2 thin film

Table 9. N/C and O/C ratios in the butadiene-N_2 thin film estimated by XPS spectra

N_2/Butadiene ratio	N/C (%)	O/C (%)
0	0	6.4
1.0	7.4	17.2
2.0	17.5	9.5
3.0	16.0	12.8
4.0	25.3	14.8
5.0	27.2	13.3
10.0	24.3	12.9

Table 10. The effect of coating by butadiene-N_2 film on the shear stress of PE joined at a steel by adhesives[a)]

N_2 flow rate (sccm)	Contact angle (°)	Shear strength (kgf/cm^2)
0	85	45
0.5	73	53
1.0	78	53
2.0	64	53
Untreated PE	102	10

a) Butadiene: 1.0sccm

6. Conclusion

The reaction mechanism of plasma polymerization is so complex that it has not been analyzed in detail yet. Therefore, to design the structure and functionality of polymerized films by controlling various conditions of plasma polymerization is quite difficult even today.

However, it is an interesting field because any chemical compound can be a candidate for polymerization monomers. Recently, active research on plasma polymerized thin films, which contain several functionalities, is carried out and many books, reviews, and patents etc. are available. 15-20)

In particular, as advanced technology, research regarding electronics devices, biocompatible biomaterials, utilizing not only combination of gas permeation membranes and diamond thin films but also combination with metal and combination with inorganic responsive gasses are carried on. Including government, private, and academic sectors, as leaders of technical innovation in future, early practical application through general research is expected.

Finally, we deeply thank to Prof. T. Yamashita and Associate Prof. Y. Yoshida of Department of Applied Chemistry, Faculty of Engineering of Toyo University for comments and instruction with this research.

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