

Formation of an adherent layer by DC plasma polymerization

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Abstract—Plasma polymerization on a metal substrate using DC glow discharge was carried out for forming an adherent layer using a hydrocarbon reactive monomer as a function of deposition time, voltage, current, and pressure. Strong adhesion of the polymerized film to the metal and high surface energy were achieved at optimum plasma discharge conditions. The surface and the interface of the polymer film were investigated by Fourier transformation Infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS). The FT-IR spectra of the polymers obtained by DC glow discharge are similar to those of the polymers obtained by RF discharge, but good adhesion of the polymer films to the metal could be obtained only by the DC discharge polymerization. The factors affecting the adhesion such as polymer damage, functional groups, and discharge conditions are investigated. Applications of the adherent layer prepared by plasma polymerization are also presented.

Keywords: DC plasma polymerization; adhesion; FT-IR; XPS.

1. INTRODUCTION

Plasma polymerization has been utilized for depositing polymeric thin films as corrosion resistant coatings [1], bio-compatible coatings [2], and hydrophilic or hydrophobic films [3]. A number of organic compounds have been investigated as monomers for plasma polymerization. Various organic compounds can be classified into two groups depending on their behavior within the discharge area. One group undergoes polymerization and other decomposes within the discharge area. Successive polymerization has been carried out using unsaturated hydrocarbons, fluorocarbons, and organosilicones, etc. [4–6]. The characteristics of polymeric films deposited by plasma polymerization depend on the deposition parameters

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Abstract

Plasma polymerization on a metal substrate using DC glow discharge was carried out for forming an adhesive layer using hydrocarbon reactive monomer in various deposition time, voltage, current, and pressure. Strong adhesion of a polymerized film on metal and high surface energy were achieved at a certain optimum plasma discharge condition. The surface and the interface of the polymer films were investigated by Fourier transformation Infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The FT-IR spectra of the polymer obtained by DC glow discharge is similar to those of the polymers obtained by RF discharge, but good adhesion of the polymer films on metal could be obtained by the DC discharge polymerization. Enhanced adhesion has been discussed in terms of polymer damages, functional groups, and discharge conditions and applications in painting and adhesion are presented.

Keywords : DC plasma polymerization, adhesion, FT-IR, XPS

1. INTRODUCTION

Plasma polymerization have been studied for depositing the polymeric thin film for growing corrosion resistive coating [1], bio-compatible coating [2], and hydrophilic or hydrophobic film [3]. A number of organic compounds have been tested as monomers for plasma polymerization. Various organic compounds could be classified into two groups depending on their behavior within discharge area. One group conducts polymerization and others decompose. Successive polymerization was carried out using unsaturated hydrocarbon, fluorocarbon, and organosilicone, etc. [4-6]. The characteristics of polymeric film deposited by plasma polymerization depends on the deposition parameters such as species of precursor, nonpolymerizable gas, polymerization mechanism, reaction temperature, gas pressure. Particularly, adhesion of polymerized film mainly depends on the species of precursor. The study on the formation of thin polymeric film on metal surface had been extensively performed by H. Yasuda [7]. Yasuda had deposited various kinds of polymeric thin film on a metal surface by RF plasma polymerization. He used monomers such as C_2H_2 , C_6H_6 , C_6F_6 , Cyclohexane, Divinyltetramethyldisiloxane, etc., and these monomers were discharged by continuous wave (CW) mode and pulse mode plasma. They found that the surface free energy of a deposited film mainly changed by species of monomers rather than by plasma mode. They reported that the polymeric films which had high surface free energy could be obtained from the monomers such as C_2H_2 , C_6H_6 and the polymeric films which had low surface free energy could be obtained from the monomers such as Cyclohexane, Hexamethylsilane, and Hexamethyldisiloxane by CW mode plasma. The physical properties of the deposited film by pulse mode plasma were not much different with those of the deposited film by CW mode. Though various kinds of polymers could be deposited on the substrate by RF plasma, the polymerized film by RF plasma degraded by time evolution and adhesion to the metal surface is not good. While,

plasma polymerization process by dc plasma, though polymerization is very difficult on the insulator surface due to a charging effect, has several merits like simple experimental system, low cost for constructing the system, and good adhesion between polymerized film and substrate. In plasma polymerization, though the species of monomer play a decisive role in deciding the characteristics of polymeric film, nonpolymerizable gas also plays an important role in changing the characteristics of polymeric film [7].

In this article, in order to form the adhesive thin polymeric film on metal a surface, acetylene (C_2H_2) gas was discharged by applying DC electrical field. To change the chemical and physical properties of deposited film, N_2 gas was mixed with C_2H_2 gas. N_2 gas is a nonpolymerizable gas but it reacts with C_2H_2 gas to form a nitrogen compound such as amide, amine and amino acid, etc., [8]. The effect of N_2 gas addition upon characteristics of the deposited film was surveyed by Fourier transformation infrared spectroscopy (FT-IR) and x-ray photoelectron spectroscopy (XPS). FT-IR and XPS spectra shows that some functional groups formed and the concentration of these functional groups is closely related with gas mixed ratio of $C_2H_2:N_2$ and deposition time. Several applications of acetylene plasma polymerized film are also presented.

2. EXPERIMENTAL DETAILS

In order to form thin polymeric film on a metal surface, DC plasma polymerization process was adopted. Figure 1 shows schematic diagram of DC plasma polymerization system used in this experiment. In order to survey the characteristics of polymeric film deposited by DC plasma polymerization, Al plate ($10 \times 10 \text{ cm}^2$) was used as a substrate material. Al substrates were directly used as an anode and a cathode electrode. Each electrode was positioned at the middle of the discharge chamber as shown in Figure 1. The separation distance between an anode and a cathode

was fixed at 10 cm. A reaction chamber was evacuated by a rotary pump, a booster pump and a diffusion pump. After a reaction chamber was evacuated below 1×10^{-5} Torr, a main gate valve was close, that is, the main chamber was isolated. The working pressure was controlled by introducing a monomer gas and a nonpolymerizable gas and was measured by BARATRON gauge (MKS, PDR-D-1) in order to measure the pressure more precisely. BARATRON gauge measures the pressure by mechanical mechanism so that it is not so much affected by the species of gas as the other vacuum gauge. The gas mixture ratio was determined by measuring the vacuum pressure. A monomer gas was introduced until the pressure of a chamber reached to certain value and subsequently nonpolymerizable gas introduced until the chamber pressure reached to predetermined working pressure. The DC plasma was initiated by applying bias to the electrodes. Applied bias was change from 0.6 kV to 1 kV. The film thickness was controlled by adjusting deposition time. The deposition time was changed from 0 to 5 min.

The chemical structures of deposited films on an anode and a cathode were surveyed by FT-IR and XPS. In FT-IR, most commonly used method for obtaining the spectra is to detect the transmitting signal at the backside of the samples. However, in this experiment, it is impossible to obtain the spectra using such a method because IR cannot penetrate metal substrate. So reflection method was used in this FT-IR study. In reflection method, IR beam is incident to the surface near parallel to the surface plane. A Perkin Elmer x-ray photoelectron spectrometer with un-monochromatized X-ray source ($\text{Mg K}\alpha = 1253.6 \text{ eV}$) was used for characterizing the deposited film. Emitted core-level electrons were collected at 30° take off angle from the substrate normal, with concentric hemispherical analyzer.

3. RESULTS AND DISCUSSION

3. 1. FT-IR study on the polymeric films deposited on an anode and a cathode

The polymeric film can be polymerized both at the anode and the cathode by applying DC bias in order to form the plasma. The polymeric films polymerized at the anode and the cathode have different properties. The ions, radicals, excited molecules and free electrons consisting of the plasma are polymerized on the electrodes depending on their polarity. Negatively charged particles and the free electron in the plasma are attracted to the anode, while positively charged particles are attracted to the cathode. That is, different kinds of energetic particles are polymerized at the anode and the cathode. Therefore, the polymeric films deposited on the anode and the cathode have different properties, which can be confirmed by the FT-IR (BRUKER. IFS120HR) analysis. Figure 2 shows the FT-IR spectra of the polymerized films on aluminum samples at the cathode and the anode. The samples are obtained by discharging the mixture gas of acetylene and nitrogen for 1 minute (total pressure = 0.3 Torr, applied power = 200 W, acetylene : nitrogen = 5:5). The peak shapes of the polymerized film are very similar with those of polyethylene. If acetylene monomer is identically polymerized, it forms polyethylene. Therefore, we can expect that the polymerized film have very similar structure with polyethylene. However, plasma discharge changes the monomer structure resulting in forming various kinds of radicals and ions. Further more, an addition of nonpolymerizable gas (N_2) also changes the structure of polymerized film. For these reasons, several FT-IR peaks that were not observed from the pure polyethylene were observed from the deposited films. The FT-IR spectra of deposited film show that there is a large difference between the two samples according to their positions. As shown in the spectra, a largest peak of the anode polymer is appeared at approximately 2930 cm^{-1} , which is generated by CH_2 stretching and CH_2

deformation oscillation and observed typically in the polymer such as polyethylene. It implies that the polymerized layer has a similar structure with polyethylene. However, in the case of the polymer deposited on the cathode, a largest peak is observed between $1700\sim1400\text{ cm}^{-1}$. In this region, the peaks originated from the oscillations by the bond between carbon and oxygen such as carbonyl ($\text{C}=\text{O}$) or the peaks originated from nitrogen compounds such as amide, amino, amine such as $\text{C}=\text{O}$ and $\text{C}-\text{N}$ are repeatedly shown. In a cathode, a peak around 2930 cm^{-1} is not remarkable, differently from the anode side. It implies that the hydrogen bonding of carbon is much reduced in the polymer at the cathode side. That is, the acetylene plasma formed various types of ions and the different types of ions are moved to and polymerized at the anode and the cathode. Particularly, in the case of the cathode, it implies that a layer that is remarkably different from acetylene is polymerized. Another strong peak is shown at the range of 3400 cm^{-1} . This peak includes O-H group and N-H group. Another difference between the anode layer and cathode layer is the peak strength of CH_2 rocking motion in aliphatic hydrocarbon. A peak shown around 710 cm^{-1} by the CH_2 rocking motion is relatively weaker both at the anode side and the cathode side than a peak around 710 cm^{-1} of original polyethylene. The absorption is not strong in the region between 710 and 750 cm^{-1} due to CH_2 rocking. The peak is a characteristic peak from a straight chain of four or more methylene groups [7]. This peak is relatively weak in the plasma polymer because a highly branched hydrocarbon chain is formed. A CH_2 stretching peak ($\sim 2930\text{ cm}^{-1}$) and a CH_2 bending mode peak ($\sim 1400\text{ cm}^{-1}$) in FT-IR spectra indicate that a highly branched but basically hydrocarbon based polymer is formed. Here, it is notable that a ratio of the CH_2 stretching band at 2930 cm^{-1} to the CH_2 rocking band at 710 cm^{-1} is much greater at the anode than the cathode. It implies that, although the hydrocarbon based-polymer is polymerized, the anode side has a more highly cross-linked structure than the cathode side. Such a result shows that the different types of polymers are polymerized according to the substrate position.

Yasuda studied the plasma polymerized film deposition on the metal inserted between the anode and the cathode by a glow discharge polymer of acetylene and have found that FT-IR signals assigned to a carbonyl region (ketone and aldehyde are generally absorbed at $1665\sim1740\text{ cm}^{-1}$) were increased. They also found that largest peak was a hydroxyl O-H bond stretching band ($3200\sim3600\text{ cm}^{-1}$) which was larger than the CH_2 stretching signals (about 2900 cm^{-1}) and a concentration of the free radical is decreased by elapse of time. When the concentration of the free radical has been measured by electron spin resonance (ESR) for 15 months, it was reduced to 87% [7]. Reduction of the free radical is very slowly progressed like oxidation of the polymer. It means that the radical is stable and oxygen is not infiltrated into the layer. Accordingly, stability of radicals and non-infiltration of oxygen is due to the highly branched and highly cross-linked network. The existence of the highly branched network can be recognized by the infrared spectra without a signal from a methylene chain. Therefore, the glow discharge polymer of acetylene is the highly cross-linked and highly branched hydrocarbon polymer including the free radical of high concentration. When the films are exposed to the atmosphere, free radicals existing on the surface are reacted with oxygen resulting in formation of carbonyl and hydroxyl groups.

3. 2. Effect of a Change in Gas Mixture Ratio

Figure 3 illustrates the FT-IR spectra examined by changing a mixture ratio of acetylene and nitrogen. As shown in Figure 3, as the concentration of nitrogen is increased, the peaks between 1700 and 1400 cm^{-1} by the bonds of $\text{C}=\text{O}$ and $\text{C}-\text{N}$ are relatively increased, as compared with the peaks at about 2930 cm^{-1} by the $\text{C}-\text{C}$ stretching. A peak at about 1700 cm^{-1} is deemed a peak by the bond of $\text{C}=\text{O}$ (aldehyde or ketone). A peak between 1660 and 1600 cm^{-1} may be a peak by the bonds of $\text{C}-\text{N}$, $\text{C}=\text{O}$ (amide, amino acid) and $\text{N}-\text{H}$ (amine, amide). A peak at about 1400 cm^{-1} is a

peak by C-H or N-H bending. As illustrated in Figure 3, it is noticeable that the strength of a peak between 1700 and 1630 cm^{-1} is much varied when the concentration of nitrogen is increased. As the concentration of nitrogen increased, the peak intensity at about 1630 cm^{-1} gradually increased. It implies that the peak at about 1630 cm^{-1} is related with a nitrogen compound, such as amino acid, amine and amide. These nitrogen compounds act as a functional group, which affects the physical or chemical properties of polymeric films. That is, as a ratio of nitrogen in a mixture gas increased, the concentration of functional groups increased.

3. 3. XPS Analysis

In general, FT-IR and XPS have been widely used as analysis methods for analyzing the polymer composition and examining its chemical state. In XPS measurement, an XPS spectrometer having a un-monochromatized Mg $K\alpha$ source is employed to compare an element ratio of C, N and O of the polymer formed by the plasma polymerization. The concentration of the films was determined by measuring the peak area under the consideration of a sensitivity factor of each element by an irradiated X-ray.

Figure 4 illustrates the XPS spectra obtained from the polymer at the anode side by the DC discharge for 1 minute (pressure = 0.3 Torr, applied power = 200 W, acetylene : nitrogen = 5:5). Although the layer is polymerized from the acetylene and nitrogen gas plasma, a large amount of oxygen is detected. It is thus inferred that oxygen does not exist in a supplied mixture gas, but may remain in the vacuum chamber and join the reaction. It is also considered that the radicals formed during the plasma polymerization are reacted with oxygen having strong reactivity and form the oxygen compounds when exposed to the atmosphere. As shown in C1s spectra of Figure 4a, the C-C bond or C-H bond that most hydrocarbon polymers contain appeared at a position of 285 eV. In

the case of a layer formed by the plasma polymerization, the position of the C1s peak is identical to 285 eV, but the peak forms an asymmetry shape. The asymmetric property results from the bond of carbon and oxygen or carbon and nitrogen, such as C-O, C=O, C=O-O and C-N. The peaks assigned to C-O, C=O, C=O-O and C-N appeared at higher than 285 eV so that the peak shape becomes asymmetric. It implies that the layer includes the functional group.

Figure 5 shows the change of atomic concentration of C, O and N calculated using XPS spectra obtained from the polymerized films. The polymeric films were deposited on the anode for 1 minute with varying the mixture ratio of acetylene and nitrogen under the conditions of a total pressure of 0.3 Torr and applied power of 200 W. The concentration of oxygen is little influenced by gas mixture ratio, while the concentration of nitrogen is dependent upon its mixture ratio. It implies that oxygen in the polymer comes from an external. In addition, the increase of nitrogen shows that nitrogen gas that is introduced in the form of mixture gas directly join the reaction. Such a result is identical to above described FT-IR results that the peak intensity related with nitrogen compound increased.

The results of the FT-IR and XPS shows that oxygen exists in the polymer and the mixture ratio of the nitrogen gas supplied for the polymerization remarkably influences on a property of the polymerized layer. Such an oxygen or nitrogen compound serves to change the characteristics of polymer. Particularly, nitrogen directly joins the reaction and changes the property of the polymer.

3. 4. Application of plasma polymerized film

Plasma polymerized film can be used as an adhesive layer among the heterogeneous materials. Particularly, adhesion of rubber to steel is of considerable practical importance in many areas of technology. However, direct adhesion of natural rubber to metal is very poor. As a result, metals

are frequently plated with brass, to which rubber adheres very strongly, or else the metals are coated with primers and adhesive [9]. Plasma polymerized acetylene film can be used as an adhesive layer between steel and rubber. In the tire industry, in order to enhance the durability, a steel wire is inserted into a rubber. In this case, adhesion of rubber to steel enormously affects the durability. In order to enhance adhesion, polymeric thin films were coated on the surface of steel wire by plasma polymerization (pressure = 0.3 Torr, applied power = 200 W, acetylene : nitrogen = 5:5). Figure 6 shows the SEM images of interface between steel wire and rubber remained on the steel wire after failure occurred by a tensile test. Though small amount of rubber coverage observed on failure surface of as-received steel wire, Figure 6(a) shows that the rubber does not bond with steel wire. While, Figure 6(b) shows that rubber coverage adheres well on failure surface of steel wire that is coated with acetylene film. It means that failure had taken place within the rubber rather than at the interface. From this experiment, we can conclude that the acetylene polymerized film can be used adhesive layer between rubber and steel.

Another important application is to offer a suitable layer for painting. Painting on a metal or plastic surface using commercial purpose paint is not easy due to low adhesion between the painted layer and the metal or plastic surface. Widely used methods are to add the chemical agents or to coat the primer layer before painting. Some of the chemical agents used as additives and organic solvent for coating the primer layer are very toxic so that it induces the environmental pollution. While plasma polymerization does not use such toxic agents and solvents, it could reduce the pollution and offer suitable layer for painting. The possibility of the polymeric layer deposited by DC plasma polymerization can be used as an interlayer for paint was examined by peel test. Peel test was performed using the scotch tape methods. However, the adhesion strength of scotch tape to painted layer is not so strong enough to show distinct difference between bare Al plate and plasma polymerized Al plate. In order to observe the difference by scotch tape test, the surfaces of painted

layer were divided into small square ($1 \times 1 \text{ mm}^2$) by a knife. Figure 7 shows the results of peel test by scotch tape. As shown in Figure 7(a), large parts of painted layer were detached from the surface of bare Al plate. While, the painted layer on a polymeric layer on Al plate by plasma polymerization were not detached by peel test {Figure 7(b)}. It means that the polymeric layer can replace the primer layer.

The enhanced adhesion in rubber/metal system and paint/metal system is related with the functional groups formed on the surface of polymeric film deposited by plasma polymerization. XPS and FT-IR results indicate that the functional groups such as C-O, C=O, (C=O)-O and C-N are formed on the surface of a polymeric layer. Many research results that these functional groups enhance the adhesion between polymer and dissimilar materials have been published [10,11]. So, it can be inferred that polymeric film deposited by plasma polymerization can be used as an interlayer for enhancing the adhesion.

4. CONCLUSION

Hydrophilic polymeric thin film could be obtained by DC plasma polymerization using gas mixture of C_2H_2 and N_2 . The characteristics of deposited films were varied by gas mixture ratio, deposition time and applied bias. FT-IR spectra show that hydrocarbon based-films similar with polyethylene structure were formed by DC plasma polymerization but the films had a highly cross-linked and highly branched network structure. In this article, we surveyed the basic characteristics of deposited film by DC plasma polymerization. However, in practical purpose, adhesion between polymerized film and metal surface is a one of most critical problems. The films deposited by DC plasma polymerization strongly adhered to an anode but they poorly adhered to cathode. So, in order to apply this technique for commercial purpose, qualitative analysis on the adhesion strength

between deposited film and metal surface should be done. We only survey the effect of addition of nitrogen gas. However, the usage of different kinds of nonpolymerizable gas species could change the resultant properties of the films so that the effect of nonpolymerizable gas such as CO_2 , H_2O , CO , NH_3 , Ar , etc., should be examined. In this article, we also show several applications of plasma polymerized film, but do not show qualitative data. The detail qualitative data will be presented for further paper.

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Figure captions

FIGURE 1. Schematic diagram for a DC plasma polymerization.

FIGURE 2. FT-IR spectra of polymerized films on a cathode side and an anode side by DC discharge of acetylene (50%) and nitrogen (50%) gas mixture. Applied power and total vacuum pressure were 200 W and 0.3 Torr, respectively.

FIGURE 3. FT-IR spectra of polymerized films. Each spectrum obtained from the polymerized film on an anode and a cathode with different gas mixture for 1 min. The plasma was discharged under the conditions of applied power of 200 W and vacuum pressure of 0.3 Torr.

FIGURE 4. XPS core level spectra of polymerized films on anode (applied power = 200 W, vacuum pressure = 0.3 Torr and acetylene : nitrogen = 5 : 5).

FIGURE 5. Change of atomic concentration of polymeric films depending on the gas mixture ratio.

FIGURE 6. SEM images of interface between steel wire and rubber remained on the steel wire after failure occurred by a tensile test. (a) as-received wire and (b) polymeric film coated wire.

FIGURE 7. Results of peel test by scotch tape. (a) paint on bare Al plate and (b) paint on polymeric film coated Al plate.