Surface Treatment of Polymer Materials and Transparent Conductive Films

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A new possibility of our atmospheric cold plasma torch has been examined on the surface treatment of an air-exposed vulcanized rubber compound. The plasma treatment effect was evaluated by the bondability with another rubber compound using a polyurethane adhesive. The adhesion property was improved by the treatment with plasma containing oxygen radicals. The oxygen radical generation from the plasma was verified and its efficiency was found to be dependent on the cathode material.

Keywords : plasma treatment, transparent conductive oxide, rubber surface, low temperature, oxygen radical, contact angle, adhesion

1. INTRODUCTION

Vulcanized rubber compounds are generally recognized to have such low surface free energies that a surface pretreatment is required to improve their adhesion property with other materials. The methods employed to increase the surface free energy of rubber compounds are mechanical roughening, exposure to flames, and surface treatments with corona discharge and glow discharge plasmas. The improvement in adhesion by the plasma treatments was attributed to surface roughening[1], surface oxidation[2] and formation of functional groups onto the surface[3,4]. Plasma employed for the treatment of vulcanized rubber compounds and silicon rubber[5] were corona discharge and glow discharge. However, these methods are normally conducted in confined areas of chamber. Recently, we developed an atmospheric cold plasma torch, which could feed chemically exited species into open air. This is especially useful for surface modification of materials, which are hardly processed in a vacuum chamber. In this study, vulcanized rubber compound surfaces were treated by the atmospheric cold plasma torch to improve adhesion properties with each other as well as with other materials, and applied to the etching of transparent conductive oxide(SnO_2) films. The treated surfaces were characterized by the contact angle measurement and adhesion.

2. EXPERIMENTAL

A vulcanized rubber of NR(natural rubber)-SBR(styrene-butadiene rubber) compound was used as the specimen. The rubber was molded into sheets of 2 mm in thickness and vulcanized by hot pressing at 140 ° C for 30 min. The SnO_2 films (ASAHI GLASS) was deposited using a RF sputtering system. The thickness and resistance of SnO_2 films was 0.3 μm, 26/□, respectively. The setup of the cold plasma torch is schematically illustrated in Fig. 1.

The plasma torch is composed of an rf powered Pt, Pd, SUS needle electrode (1 mm in diameter and 30 mm in length) and a grounded cylindrical stainless-steel electrode (5 mm i.d. and 20 mm in length) whose inside is covered with an alumina tubing (0.5 mm in thickness).

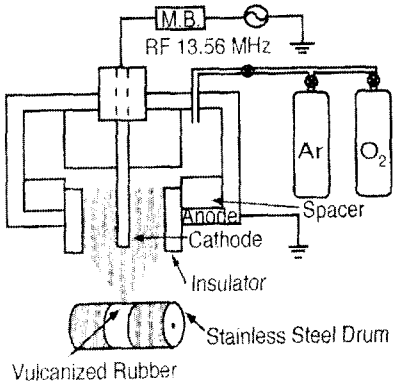

Fig.1. A schematic diagram of cold plasma torch system.

The discharge plasma of O_2, H_2 and CH_4/Ar (300 sccm) was generated by applying 70 W and 90W rf power between the electrodes and was exhausted into air. The rubber sheets were glued on a SUS drum (100 mm in diameter) rotating at 8 rpm and placed 2 mm away from the plasma outlet to be exposed to the discharge for 50 s. The contact angle of vulcanized rubber surface with pure water was measured at room temperature using an KYOWA contact-angle meter CA-D for evaluating the wettability of the rubber surface. The rubber sheet and a chlorinated rubber sheet as a reference were bonded with a polyurethane adhesive. The sandwich structure was held in a grip at room temperature for 2 days. Since the chlorinated rubber is known to bond tightly with the polyurethane adhesive, this force was used as a measure of the bondability of the plasma treated or untreated rubber surface with the adhesive. The peel force was measured by a SHIMADZU (AGS-100D) tester at a crosshead speed of 10 mm/min at room temperature. The optical emission of an emerging plasma beam was transferred through an optical fiber and recorded by a JASCO CT-25C spectrometer in the range of 400 nm to 850 nm with 0.1 nm spatial resolution. The O* (844.6 nm)/Ar* (750.4 nm) emission intensity ratio is used for quantitative evaluation of the oxygen radical flux[6]. Radical flux was measured quantitatively by the quartz crystal micro-balance (QCM) method[7]. On a quartz crystal sensor of 1.4 cm diameter, a silver (Ag) film was evaporated as thick as 400nm. The Ag coated quartz sensor was placed in an oxygen containing plasma to increase its weight as the Ag film reacted with oxygen radical to form AgO. The radical flux was evaluated by using the frequency to mass conversion factor of 1.56 x 10^{-7} g/cm^2 x Hz. The Ag coated quartz crystal sensor was placed 2-4 mm away from the plasma outlet nozzle. Electron temperature (Te) in the plasma was determined by the I-V characteristic using a single probe method, while gas temperature (Tg) was by a thermocouple[8]. The film thickness was measured by the stylus method.

3. RESULTS AND DISCUSSION

By the plasma treatment, no appreciable change was observed in the appearance of rubber surfaces. However, there were changes in adhesion force with urethane adhesives as shown in Fig. 2.

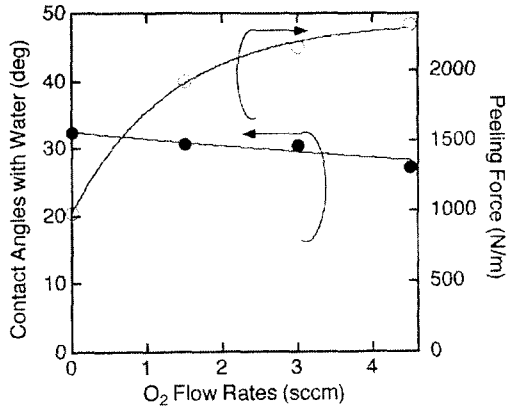

Fig. 2. The contact angles with water and peeling force of vulcanized rubber after the plasma treatment. The contact angles and peeling force of untreatment rubber were 108.5 ° and 280N/m, respectively.

The untreated rubber surface showed a hydrophobic property whose contact angle was 108.5° . The contact angle decreased by the plasma treatment using higher O_2 flow rate, thus wettability was improved by the oxygen plasma treatment. The adhesion force was improved by the treatment of oxygen containing plasma. When the rubber was treated with plasma at an O_2 flow rate of 4.5 sccm, the peeling force (2322 N/m) reached seven times as high as that of untreated rubber assembly. The atmospheric plasma was generated in the space between the needle cathode and alumina tubing and blown out from the alumina tubing. Typically, plasma was generated by applying an rf power 70 W to the cathode in the Ar (300 sccm) flow containing oxygen (0-4.5 sccm). The emissive plasma beam generated has 4 mm diameter and a length variable from 1 to 5 mm depending on the gas flow rate. Te and Tg in the plasma at an O_2 flow rate 4.5 sccm were evaluated to be 1.2 eV and 44.2 meV (240 ° C), respectively, indicating a non-equilibrium glow discharge type of the plasma. Emission lines from Ar and N_2 were clearly detected in the wavelength range between 400 nm and 700 nm in the plasmas of Ar with and without O_2 mixing. No other emission line was detected in this range.

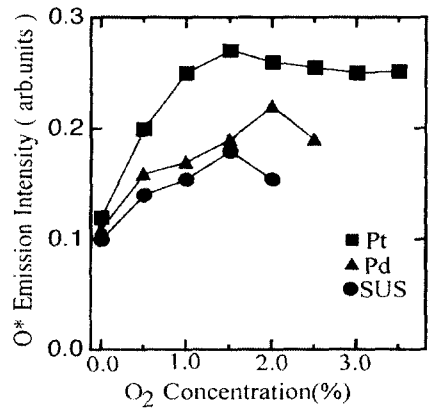

Fig. 3. The O* emission intensity as a function as a function of O_2 concentration at 70 W rf power.

The decomposition of O_2 was confirmed by the presence of O* line at 777.4 nm and 844.6 nm in the spectra of O_2/Ar plasmas. The O* (844.6 nm)/Ar* (750.4 nm) emission intensity ratio was used for quantitative analysis of oxygen radical[6].

Fig. 3 shows the O*(844.6 nm)/Ar*(750.4 nm) emission intensity ratio to generate plasma plotted as a function of O_2 concentration in Ar flow by applying 70 W rf power.

The relative O* emission intensity increased with the increase of O_2 concentration from 0.5 to 2.0 % to reach the maximum and decreased with further increase of

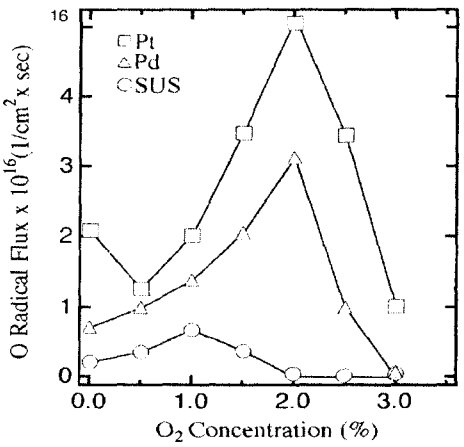

Fig. 4. The oxygen radical flux as a function as a function of O_2 concentration at 70 W rf power.

O_2 concentration. The O* emission from the plasma using a Pt cathode was higher than that using a stainless steel or Pd cathode of the same size. The plasma was flashed to Ag film deposited on a quartz sensor. The sensor frequency decreased gradually, indicating an increase in mass due to the Ag film oxidation. Flashing the Ag coated sensor with O_2/Ar gas without igniting plasma gave no change in the quartz frequency. Thus, Ag was oxidized only by oxygen radicals in the plasma to be converted into AgO. The oxygen radical flux evaluated by using this QCM method is detected in Fig. 4 as a function of O_2 concentration in the plasma gas (Ar). The oxygen radical flux increased with the increase of O_2 concentration from 0.5 to 2.0 % and decreased with further increase of O_2 concentration. Under the conditions of 1.5 % O_2 in Ar 300 sccm and rf power 70 W, the oxygen

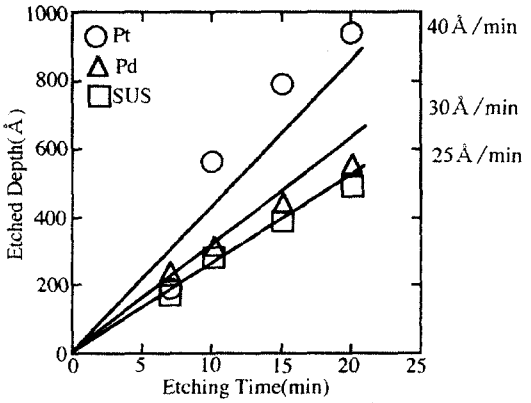

Fig. 5. Etched depth of SnO_2 as a function of etching time.

radical flux reached 3.5 x 10^{16} /cm^2 x sec by using a Pt cathode, more than 9.6 times higher than the radical flux produced by using a stainless-steel cathode. From the comparison Fig. 3 with Fig. 4, we can see a parallel relationship between the oxygen radical flux determined by the QCM method and O* emission intensity. Although the etching rate was relatively low as compared with the etching in vacuum[9,10], SnO_2 etching in Fig.5 did occur even in air by using our system under same etching conditions, the etching rate using Pt cathode was twice as high as that using stainless-steel cathode. This tendensy was in parallel with the cathode material dependence of H_α* (656 nm) and CH*(430 nm) emission intensity in the plasma.

4. CONCLUSION

Vulcanized rubber surfaces were treated with Ar and O_2/Ar cold plasma torch in air. The increase in the O_2 flow rate in the plasma gas resulted in the increase in the amount of oxygen radicals. Under the conditions of 1.5 % O_2 in Ar 300 sccm and rf power 70W, the oxygen radical flux increased to 3.5 x 10^{16}/cm^2 x sec by using Pt

cathode, which was more than 9.6 times higher than the radical flux achieved by using the stainless-steel cathode. The atmospheric pressure cold plasma torch has such a low Tg that it is useful for plasma modification especially of air-exposed surfaces of both inorganic and organic materials. SnO_2 etching did occur even in air by using our system. Under same etching conditions, the etching rate using Pt cathode was twice as high as that using Stainless-Steel cathode.

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