Surface Treatment of Transparent Conductive films and Polymer Materials

Bong-Ju Lee[1], Hyun-Kyu Lee[2], Soo-Bok Chung[3], Kyung-Sub Lee[4], Hyung-Kon Kim[5], Hyoan-Ki Chung[6]

1)Division of Physics and Chemistry, College of Nature Science, Chosun University
2)Division of Metallurgical and Materials Engineering, College of Engineering, Chosun University
3)Division of Electrical And Control & Instrumentatin Engineering, College of Engineering, Chosun University
4)Division of Electrical and Electronics Engineering, College of Engineering, Dong-Shin University
5)Department of Electrical Engineering, Chosun College of Science & Technology
6)Korea Electric Power Corporation

Abstract

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.

Key Words : plasma treatment, rubber surface, low temperature, oxygen radical, atmospheric pressure, 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. Among 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 1,2), surface oxidation3) and formation of functional groups onto the surface4,5). Plasma employed for the treatment of vulcanized rubber compounds6) and silicon rubber7) 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. The treated surfaces were characterized by the contact angle measurement, 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 setup of the cold plasma torch is schematically illustrated in Fig. 1. The plasma torch is composed of an rf powered Pt 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 (0.5mm in thickness). The discharge plasma of O_2 (0-4.5 sccm) / Ar (300 sccm) was generated by applying 70 W 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. Contact angle of water on vulcanized rubber surface 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.

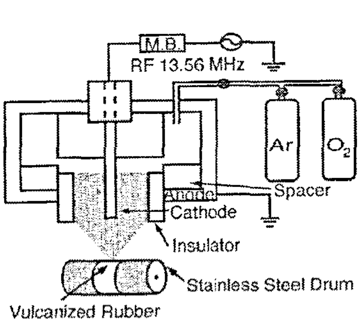

Fig.1. A schematic diagram of cold plasma torch system.

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. 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 oxygen containning 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

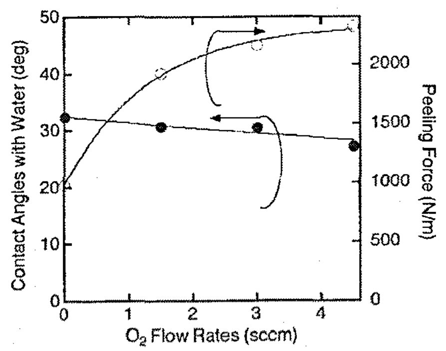

Fig. 2. The contact angles with water and peeling force of vulcanized rubber after the plasma treatment. The contact angles and peeling force of untreatment rubber were 108.5 ° and 280N/m, respectively.

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 1.2eV and 44.2 meV (240 °C),

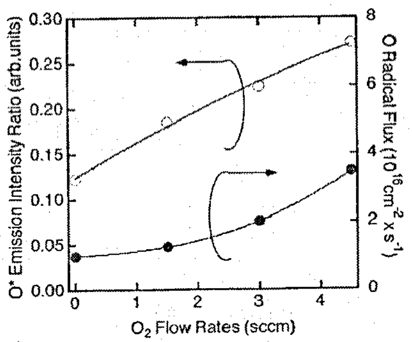

Fig.3. O^*(844.6nm)/Ar^*(750.4nm) emission intensity ratio and oxygen radical flux as function of O_2 flow rate.

respectively, indicating a non-equilibrium glow discharge type of the plasma. Emission lines from Ar and N_2 were clearly detected in the range of 400 nm to 700 nm in the plasmas of Ar with and without O_2 mixing. No other emission line was detected in this range. Figure 3 shows the variation of O^* (844.6 nm) and Ar^* (750.4 nm) emission intensity ratio and the oxygen radical flux as a function of O_2 flow rate mixed in a constant 300 sccm Ar flow. Both emissive and oxidative oxygen radicals increased their concentrations with the increase of O_2 flow rate.

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. After the treatment, rubber surfaces were physically and chemically modified to improve the wettability of rubber surfaces and adhesive properties. 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.

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