Pre-treatments of polymers by atmospheric pressure ejected plasma for adhesion improvement

Jong-kyu Park*, Won-tae Ju*, Kwang-hyun Paek*, Yong-hwan Kimb, Yoon-ho Ch oib, Ji-hun Kimb, Yong-seok Hwang*

*Plasnx. Co. Ltd, Seoul 151-744, South Korea
bDepartment of Nuclear Engineering, Seoul National University, Seoul 151-744, South Korea

Abstract

Polymers such as rubbers generally have low surface energy, thus high hydrophobicity and inherent low bondability. An atmospheric pressure ejected plasma (APEP) source is developed for pre-treatments of polymers to overcome these intractable properties and improve the adhesion ability between polymers as environmental-friendly and simple alternative methods to conventional treatments in spite of several limitations until now. Proper operational conditions are found by T-peel tests performed with various plasma parameters and high peel strength up to 3.5 kgf/cm is achieved at those conditions. Optical emission spectroscopy revealed that the amount of oxygen radicals and gas temperatures are found to be higher at proper conditions in T-peel tests and Fourier transform infrared spectroscopy using attenuated total reflection. Scanning electron microscopy is used for the measurement of surface composition and morphology of pre-treated polymer specimen. These results established the advantage of pre-treatments by APEP source in proper operation conditions when compared to the conventional treatments in terms of improvement of the adhesion ability between polymers.

Keywords: Plasma; Atmospheric pressure; Polymers; Adhesion; T-peel test

1. Introduction

Plasma treatments have been suggested as an alternative method for the adhesion improvement of polymers because of its environmental-friendly characteristics when compared to other conventional surface treatments. Several studies report that reactive radicals and energetic particles included in plasma can change the characteristics of surfaces and improve the adhesion ability in results of [1–3]. But these vacuum-based treatments are too expensive, complicated and slow to be used in real industrial application.

Atmospheric pressure ejected plasma (APEP) source has been developed not only to overcome these problems of batch type process [4], but also to improve other atmospheric plasma source limitations. In this article, styrene butadiene rubber (SBR) and pylon produced from EVA commonly used in footwear manufacturing process are used to validate the ability of adhesion improvement of APEP source. In real application, for example, SBR and pylon are used as outsole and midsole, respectively, and adhesion strength of two polymers are demanded to be more than 2.5 kgf/cm in results of T-peel tests. To find the proper conditions of APEP source, several operational parameters such as gas composition, species, flow rates, RF power and process time are investigated by T-peel tests. Plasma parameters are also measured especially to study the relationship among performance, radical contents and gas temperature and treated surface of polymers are analyzed to investigate the change of chemical composition and morphology of the surface. From these experiments and results, it is suggested that the extended APEP source with the larger size has the larger capability of improving the adhesion ability of polymers developed.

2. Experimental

APEP source has a coaxial shape composed of two electrodes, ceramic insulator between the electrodes, gas
distributor for the ejection of plasma and coolant pass structure as shown in Fig. 1. Stainless steel electrode was determined as hot electrode material for comparatively high gas temperature and 27.12 MHz RF power was supplied for the same reason [4]. Helium and argon gas is used as carrier gas to generate and extract plasma; oxygen and nitrogen gas is used as reactive gas to generate radicals necessary to improve the adhesion ability of polymers. To increase radical contents in plasma, helium and argon gas ratio was fixed as 1:0 or 1:1 [4] (Fig. 2).

With various operational parameters, T-peel tests of adhesive joint between SBR and pylon were performed according to the following procedure. As a primary treatment, the surface of polymers was wiped with water, methyl ethyl ketone solution and dried in the desiccators at the temperature of 60 °C for approximately 7 min. After plasma treatments, aqueous polyurethane adhesive manufactured by Dong Sung NSC co. Ltd, was applied with a brush and desiccated for approximately 7 min again. After adhered to each other, SBR and pylon was pressed for approximately 10 min and conditioned properly for 24 h before undergoing the T-peel tests.

O* intensity for oxygen radical contents and ultraviolet OH lines for gas temperature are measured by optical emission spectroscopy (OES). Fourier transform infrared spectroscopy using attenuated total reflection (FTIR-ATR) measurement for surface composition analysis is performed in the wavelength range of 400–4000/cm and scanning electron microscope (SEM) is used to scan the morphology of the treated surfaces.

3. Results and discussions

3.1. Determination of proper conditions of APEP source by T-peel tests

After pre-treatments of SBR and pylon using APEP source with various parameters such as gas composition, flow rates, RF power and process time, T-peel tests were performed to find proper operational conditions for the adhesion ability.

Fig. 3 shows that the adhesion ability can be improved considerably with He/O and Ar/He/N gas composition. But, these effective gas compositions are dependent on treated specimen because of the complexity of interactions between the radicals in plasma and the surface of treated polymers. He/O2 plasma treatment to SBR and Ar/He/N2 plasma treatment to pylon, in APEP
source, are not proper as revealed from these experiments. Fig. 4 shows that the adhesion strength increases with power but decreases above the specific power; 200 W in case of He/O\textsubscript{2} plasma and 100 W in case of Ar/He/X\textsubscript{2} plasma. This can be explained easily because oxygen radical contents also increase with power and these radicals, especially oxygen radicals, have an important role in the adhesion [4], but surface may be damaged or plasma become unstable with excessive power. For the same reason, the adhesion strength can be maximized when polymer specimen is treated in proper processing time shown in Fig. 5. With those proper conditions, higher peel strength (> 3 kgf/cm) could be achieved in APEP source than that reported in other papers [1,2].

3.2. Oxygen radical contents and gas temperatures in APEP source

The experimental results in Fig. 3 may be related to radical contents in plasma. Therefore, it is necessary to conduct the experiments with varying reactive gas flow rates. Higher radical contents are expected when the reactive gas flows are as large as possible. However, Fig. 6 shows that the proper gas flow rates for maximum peel strength exist so that peel strength decreases above the proper gas flow rates. There are two possible explanations for this result; oxygen radical contents are not proportional to oxygen gas flow rates or the radical contents do not have simple relationships with the adhesion ability. OES measurement for oxygen radical contents in Figs. 7 and 8 show that the former explanation is more adequate. In the case of He/O\textsubscript{2} plasma, oxygen radical contents are not proportional to the gas flow rate and show the consistency with the peel strength results in Fig. 6 within the small error ranges. In the case of Ar/He/N\textsubscript{2} plasma, a sudden drop of oxygen contents occur above the specific nitrogen gas flow rate that shows maximum peel strength. These results obviously have the meaning that oxygen radical contents play an important part in improving the adhesion ability.

Fig. 9 shows well this correlation between the two factors. However, the reasons behind the deviations in Fig. 9 cannot be passed over. Comparing oxygen radical contents of Ar/He/N\textsubscript{2} plasma with that of Ar/He/O\textsubscript{2} plasma in Fig. 8 suggests that nearly the same results can be seen at smaller reactive gas flow rate than 200 sccm, but Ar/He/O\textsubscript{2} plasma has the poor ability of improving the bondability on the contrary to Ar/He/N\textsubscript{2} plasma. This implies nitrogen radical effects may be
related in Ar/He plasma. Also, these deviations may be originated from the complicated interactions between plasma and the treated surface. Superficially, the gas flow and extraction of plasma is affected differently according to the kind of polymer used.

Fig. 10 shows gas temperature of APEP source by measurement of OH lines in OES [5]. As expected for 27.12 MHz RF and stainless steel electrode, high temperatures are measured on the whole but independent on the oxygen radical contents. In the view of the results so far, He/O₂ plasma has high gas temperature and oxygen radical contents at the proper conditions, Ar/He plasma has medium gas temperature, oxygen radical contents and other radical effects affecting on the bondability of surface.

3.3. Surface characterization of surface pre-treated by plasma by FTIR and SEM

When polymers are treated by plasma, oxidization or radical deposition and ablation are competed generally. In the respect of the surface composition changed by plasma, C=O functional groups that have an important role in improving the bondability which can be increased by oxidization, and CH₃, paraffin wax and zinc stearate that create antiadherent layers can be decreased by ablation. FTIR-ATR is used to analyze this modified surface composition by plasma and especially to identify the reason that the results of T-peel tests are different as what plasma is used or which polymer is treated. At the proper conditions of He/O₂ plasma, strong ablation by high temperature and also strong oxidization by high oxygen radical contents remove CH₃ groups mostly and increase C=O groups slightly in both polymers as shown in Fig. 11a and b. In the case of SBR surface treated by Ar/He/N₂ plasma, as shown in Fig. 11c, nearly the same results can be seen although oxygen radical contents are smaller than that of He/O₂ plasma. However, in spite of the same plasma treatment, pylon surface treated by Ar/He/N₂ in Fig. 11d shows that all groups are mostly increased at the proper condition. These results imply Ar/He/N₂ plasma treatment to
Table 1
Summary of FTIR measurements and T-peel test results from Figs. 3–11

<table>
<thead>
<tr>
<th>Plasma to SBR</th>
<th>Plasma to pylon</th>
<th>C=O in SBR</th>
<th>CH_x in SBR</th>
<th>C=O in pylon</th>
<th>CH_x in pylon</th>
<th>Bondability</th>
</tr>
</thead>
<tbody>
<tr>
<td>He/O_2</td>
<td>He/O_2</td>
<td>Slightly inc</td>
<td>Dec</td>
<td>Slightly inc</td>
<td>Dec</td>
<td>High</td>
</tr>
<tr>
<td>Ar/He/N_2</td>
<td>Ar/He/O_2</td>
<td>Slightly inc</td>
<td>Mostly dec</td>
<td>Slightly inc</td>
<td>Dec</td>
<td>High</td>
</tr>
<tr>
<td>He/O_2</td>
<td>Ar/He/N_2</td>
<td>Slightly inc</td>
<td>Mostly dec</td>
<td>Inc</td>
<td>Inc</td>
<td>High</td>
</tr>
<tr>
<td>Ar/He/O_2</td>
<td>Ar/He/O_2</td>
<td>Medium inc</td>
<td>Inc</td>
<td>Inc</td>
<td>Inc</td>
<td>Medium</td>
</tr>
</tbody>
</table>

Fig. 12. SEM photographs of treated surface with proper gas flow rate and power (a) SBR as received; (b) SBR by 2 s He/O_2 plasma; (c) SBR by 4 s He/O_2 plasma (d) SBR by 2 s Ar/He/N_2 plasma.

pylon is impertinent and explains to some extent why He/O_2 plasma treatment of SBR and Ar/He/N_2 plasma of pylon shows low peel strength in Fig. 3. As summarized in Table 1, the bondability measured by T-peel tests and FTIR analysis show a comparatively good consistency. However, interaction between the surface of polymers and plasma, especially in the light of radicals, must be investigated more in detail.

Fig. 12 shows the surface of treated polymer by SEM. Surface morphology is changed to be more smooth by He/O_2 plasma because of strong ablation and oxidation effects but damaged with excessive processing time as expected and shown in Fig. 12c. In case of Ar/He/N_2 plasma treatment, surface is not changed to be smooth and somewhat different from the case of He/O_2 plasma in spite of the similar T-peel test and FTIR results. This also suggests the nitrogen radical effects to exist.

3.4. Extended APEP source

Extended APEP source in Fig. 13b was designed to have larger nozzle to be able to deal with wider surface treatment. From the same measurement results as original type in Fig. 13a, extended type was proved to have larger plasma flame, oxygen contents and, therefore, effectiveness to improve the adhesion ability of polymers are more than the original type. At proper conditions, for example, peel strength of approximately 5 kgf/cm could be achieved.

4. Conclusions and future work

APEP source is effective to improve the adhesion ability of polymers at the proper operation conditions such as He/O_2 and Ar/He/N_2 gas composition. These conditions are dominantly dependent on oxygen radical contents but nitrogen radical effects cannot be neglected. FTIR and SEM measurements show a good consistency and support that result. Therefore, these radical effects and complicated interaction between plasma and treated polymer surface must be investigated in more detail. This ability to increase the bondability can be more improved with extended type. Still, for real commercial
applications, much larger size APEP source should be studied and developed in the long run.

Acknowledgments

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References