Surface Morphology and Chemistry Alternation of Natural Rubber Using Low Temperature Plasma Treatment

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Abstract:
Low temperature plasma was used to treat a deproteinized natural rubber (DPNR) to improve adhesion with other polymeric materials. DPNR latex was prepared using protease from bacterium Bacillus subtilis (MR10). DPNR latex was cast on a glass plate and a gauze pad and then dried at room temperature. Plasma power, plasma treatment time, and composition of the gas mixture were considered. The plasma modified surfaces were analyzed by attenuated total reflection infrared spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy. The adhesion was tested by peel testing. The argon–oxygen gas mixture at flow rate 4 L/min and 36 mL/min was optimum condition for DPNR on glass sample with power of 20W, distance between source and sample at 5 mm for 80 sec. The treatment condition of DPNR on gauze pad was used at the same flow rate of gas mixture and power. But the distance between source and sample was changed to 10 mm with treatment rate at 2 min 50 sec per 10 cm. Surface roughness change and spherical carbon bubble formation was observed. Changing of surface composition was mainly ascribed to the formation of ether linkage on the modified surfaces. Peel strength of plasma treated samples were higher than that of untreated samples about 42%.

1. Introduction
The natural rubber is of growing interest owing to its potential importance on biomedical applications. The plasma treatment of rubbers has become a strategic methodology in the development of new class of materials through graft copolymerization1-3, fluorination4, blending5 and layer-by-layer6 deposition. These methodologies have provided improvements on chemical resistance7 and antibacterial properties of latex medical glove7 as well as on interfacial adhesion8. However, no improvements on mechanical properties are reported as consequence of plasma treatment and the best results related to improvements on hydrophobic properties report contact angles ranging from 103 to 119°.4,7

In this research, plasma was used to promote the adhesion between two surfaces because it can create the chemically active functional groups such as amine (-NH2), carbonyl (-C=O), and hydroxyl (-OH) groups to improve interfacial adhesion.8 The surface modified by oxygen and nitrogen plasma can improve adhesive properties resulting in generation of polar groups such as –OH, -C=O, -COOH, -NH2, and -C=NH on the polymer surface which can be proved by x-ray photoelectron spectroscopy (XPS) and attenuated total reflectance fourier transform infrared (ATR-FTIR).11

This work will focus on deproteinized natural rubber (DPNR) treated with low temperature plasma for improving adhesion properties. Effects of plasma power, plasma treatment time and composition of the gas mixture on surface modification were considered. The surface free energy and surface morphology of
DPNR treated plasma were investigated. Peel testing was also studied.

2. Materials and Methods

DPNR was prepared by using protease enzyme. Protease from bacterium *Bacillus subtilis* (MR10) was prepared using the method according to Wongputtisin *et al.* Protease was added to concentrated low ammonia natural rubber (LA-NR) latex with ratio 600 unit of protease/100 ml of latex. After stirring for 5 hours, DPNR latex was obtained. DPNR latex was cast on a glass plate and then dried at room temperature.

**Figure 1** Schematic of the atmospheric pressure plasma jet configuration.

The rubber samples subjected to plasma-jet treatment at the power of 20 W with setup as shown in Figure 1. The plasma-jet system used in this experiment is similar to the previous one, described. To achieve the sample coverage, spot-like plasma jet plume was scanned over the sample area of 2.5×10 cm². The Ar/O₂ mixed gas plasma was applied for prompt generation of candidate species for surface functionalization. The argon-oxygen gas mixture at flow rate 4 L/min and 36 mL/min was optimum condition for DPNR on gauze pad with power of 20 W, distance between source and sample at 10 mm with treatment rate at 2 min 50 sec per 10 cm. Treatment time was varied at 20-120 sec. AXIS ULTRA DLD (Kratos analytical ltd, UK) was used to collect x-ray photoelectron spectrum. The base pressure in the XPS analysis chamber was about 5×10⁻⁹ Torr. The samples were excited with X-ray hybrid mode 700×300 μm spot area with a monochromatic AL Kα, 1, 2 radiations at 1.4 keV. X-ray anode current was run at 15 kV, 10 mA and 150 W. The photoelectrons were detected with a hemispherical analyzer positioned at an angle of 45° with respect to the normal to the sample surface. Attenuated total reflectance Fourier Transform Infrared (ATR-FTIR) spectrum was measured using Thermo Scientific™ Nicolet™ 6700 FT-IR. The wave number range from 4000-550 cm⁻¹ was selected to analyze. The surface morphologies of plasma treated DPNR were studied with scanning electron microscopy (SEM) (JSM-5910LV, JEOL). The gauze pad coated was prepared for peel testing. Peel strength was tested under Thai Industrial Standard (TSI) Number 318-2552. Moreover, the low-ammonia natural rubber latex (LA-NR) was also investigated for peel testing.

3. Results & Discussion

To investigate a chemical modification, experimental characterization such as surface free energy (SFE), SEM, ATR-FTIR, XPS, and peel strength were carried out.

3.1 Surface free energy

The SFE of plasma treated rubber were determined by measuring the contact angles at a room temperature. Water contact angles have been measured before and after plasma treatments to indicate adhesive ability of the treated sample as shown in Figure 2. It was found that O₂/Ar plasma reduced the contact angle of the rubber from 50° to 20-32°. It can be explained that the surface of rubber became hydrophilic (sticky surface) after treatment. However, the contact angle increased when treatment time increasing (became hydrophobic or less sticky surface).
The SFE of untreated and plasma treated rubber determined by measuring the contact angles.

3.2 Surface morphology
Scanning electron micrographs of DPNR latex films at various plasma treatment time; 0 sec, 30 sec, 60 sec and 120 sec were presented in Figure 3. The argon–oxygen gas mixture was found to modify rubber surface morphology. Surface roughness change and spherical nano bubble formation was observed. After the treatment time of 20 seconds, spherical bubble with a radius around one micron formation was observed. The bubble size becomes greater to 5 micron up to 30 seconds. At 80 seconds, surface roughness was found significantly changed. The results indicate a deformed structure, which may due to heat accumulation in an excessively long treatment time condition.

3.3 Functional group analysis
A chemical change at the surface was carried out using ATR-FTIR, and XPS. ATR-FTIR spectrum shows almost the same fingerprint of all the samples as shown in Figure 4.

This is probably due to only trace change at the surface so that this technique cannot distinguish the modification. However, XPS can successfully be used to analyze the chemical modification as shown in Table 1 and Figure 5. Changing of surface composition was mainly ascribed to the formation of ether linkage on the modified surfaces. This result can be confirmed with surface free energy. The ether linkage (-C-O-C) increased when the time of plasma treatment increased. Nevertheless, the ether linkage decreased when the treatment time more than 80 seconds. The high formation of ether linkage has an effect on better adhesion.

3.4 Peel Testing
The adhesive of each rubber lattice were measured as shown in Figure 6. The
treated samples (LANR_T, DPNR_T) have shown the higher peel strength than that of untreated samples. It can be explained that an increase of ether linkage and surface roughness as shown in Figure 3 and Table 1. Likewise, the surface of rubber became hydrophilic (sticky surface) after treatment. Moreover, peel strength of plasma treated samples were higher than that of untreated samples about 42%.

The LANR_T was an adhesive force more than the DPNR_T cause of the influence from protein in rubber.

### Table 1: Chemical composition in the surface of plasma treated DPNR.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>%Area</th>
<th>Plasma Treatment Times (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>C-C, C-H</td>
<td>82.6</td>
<td>29.5</td>
</tr>
<tr>
<td>C-N</td>
<td>8.9</td>
<td>61.0</td>
</tr>
<tr>
<td>C-O-C, C-O-H</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C=O</td>
<td>6.0</td>
<td>11.7</td>
</tr>
<tr>
<td>O-C=O</td>
<td>2.5</td>
<td>7.8</td>
</tr>
</tbody>
</table>

**Figure 5** XPS spectra of carbon peaks from untreated and treated DPNR.

**Figure 6** Peel Strength of untreated and treated plasma on LA-NR and DPNR Latex.

### 4. Conclusion

The plasma modified rubber surfaces were analyzed by means of contact angle measurement, ATR-FTIR, XPS, and SEM. The argon-oxygen gas mixture with optimum power was found to modify rubber surface morphology. The reduction of the contact angle of plasma treated sample was found. These phenomena implied a promotion of surface radicals or creation of chemically active functional groups as described in our previous work. Surface roughness change and spherical nano bubble formation were observed. Changing of surface composition was mainly ascribed to the formation of ether linkage on the modified surfaces.

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