EFFECT OF PLASMA TREATMENT ON SURFACE PROPERTIES OF NANOSTRUCTURED CARBON BLACKS

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ABSTRACT: In this work, the surface properties of carbon blacks treated by oxygen plasma were investigated in acid-base surface value, zeta potential, and X-ray photoelectron spectroscopy (XPS). And their mechanical interfacial properties of the carbon black/rubber composites were studied by the composite tearing energy (GMC). As experimental results, it was found that the introduction rate of oxygen-containing functional groups, such as carboxyl, hydroxyl, lactone, and carbonyl groups, onto the carbon black surfaces increased as the plasma treatment time increases. It revealed that the polar rubber, i.e., acrylonitrile butadiene rubber (NBR), showed a high degree of interaction with oxygen-containing functional groups of the carbon black surfaces, resulting in improving the tearing energy (GMC) of the carbon black/NBR composites.

Keywords: carbon black, oxygen plasma, surface properties, mechanical interfacial properties

1. INTRODUCTION

Carbon blacks are important materials that have been widely used as fillers in elastomers. However unmodified carbon blacks cannot be used directly for real applications. The traditional manufacturing processes cannot always obtain the desired surface properties of carbon blacks. Therefore, the modification of carbon black surfaces by chemical or physical method, such as oxidation, plasma treatment, polymer grafting, etc., have been intensively studied [1-2].

Plasma treatment is one of the most popular treatments of carbon materials. The treatment is that the reaction takes place only on the carbon black surfaces without changing its bulk properties and the other is that it is possible to make any atmospheres, such as oxidative, reductive, inactive, etc [3]. Carbon black
surfaces by oxygen plasma treatment have been reported to enhance the reinforcement of polar rubber. Chemical reactivity of the rubber-carbon blacks is attributed to the presence of oxygen-containing functional groups, such as phenol, quinone, carboxyl and lactone [4]. In this work, the surface properties and of carbon blacks treated by oxygen plasma are investigated. The surface properties of carbon black by the oxidation process of oxygen plasma are investigated in acid-base surface value and X-ray photoelectron spectroscopy (XPS). And their mechanical interfacial properties of the carbon black/ acrylonitrile butadiene rubber (NBR) composites are studied by the composite tearing energy ($G_{\text{MC}}$).

2. EXPERIMENTAL

2.1 MATERIALS AND PLASMA SURFACE TREATMENT

Carbon blacks (N220 noted in ASTM destination) were supplied by Korea Carbon Black Co. Plasma processing for the carbon black was carried out using a radio frequency for $O_2$ gas (Tegal Plasmad®). The radio frequency (13.56 MHz) generated by oxygen plasma was operated at 60 W. The input treatment time for oxygen plasma treatment varied between 0 and 30 min, namely CB-0, CB-5, CB-10, and CB-20. The compounding formulations were reported in Table 1. For the measurement of mechanical properties of filled vulcanizates, the compounds were cured at 1.5 MPa and 160°C for 60 min.

2.2 SURFACE PROPERTIES

2.2.1 pH and Acid-Base Value

The pH of the carbon black surfaces was measured according to ASTM D3838. The acid-base values of the carbon black surfaces were determined by Boehm’s titration method [5]. In the case of acid value measurement, about 0.1 g of the samples were added to 100 ml of 0.1 N NaOH solutions and shaken for 24 h. The solutions were then filtered through membrane paper ($\Phi = 0.45 \mu$m, nylon) and titrated with 0.1 N HCl solutions. Likewise, the base value was determined by converse titration.

2.2.2 X-ray photoelectron spectroscopy (XPS)

The chemical compositions of carbon black surfaces was analyzed using electron spectroscopy (XPS VG Scientific LAB MK-II). The spectra were collected using a Mg $K\alpha$ X-ray source (1253.6 eV). The pressure inside the chamber was held below $5 \times 10^{-8}$ Torr during analysis.

2.3 MECHANICAL INTERFACIAL PROPERTIES

The tearing energy ($G_{\text{MC}}$) [6] which was one of the critical strain energy release rate ($G_C$) was characterized by trouser beam tests for the mechanical behaviors of rubber compound composites. Rectangular specimens with dimensions of about 70 mm long, 50 mm width, and 2 mm thick were cut
from a sheet that were manufactured by a two-roll mill technique. All tests were conducted at a crosshead displacement rate of 2 mm/min.

3. RESULTS AND DISCUSSION

3.1 SURFACE PROPERTIES

3.1.1 pH and Acid-Base Value

Table 2 shows the results of pH and acid-base values of carbon black surfaces during the oxygen plasma treatments. As experimental results, acid-base values of the plasma treated carbon blacks are increased as a function of the plasma treatment time. This is due to a number of factors, including an increase in acidic and basic functional groups, oxidized groups, and free radicals. In this work, the degree of acid value increasing with treatment time shows higher than that of basic value of carbon blacks, resulting in decreasing the pH value of carbon black surfaces. The result indicates that the increasing of oxygen-containing functional groups, especially acidic functional groups, leads to an increase of the acid value on carbon black surfaces.

3.1.2 X-ray photoelectron spectroscopy (XPS)

Fig. 1 shows the XPS survey scan spectra with carbon black surfaces. The surface shows carbon and oxygen (binding energy, 285 and 532 eV, respectively) peaks. The oxygen peak can be derived from the oxygen containing functional groups. Table 2 represents the XPS results of the chemical compositions of oxygen plasma-treated carbon black surfaces. As a result, the content of oxygen and the O$_{1s}$/C$_{1s}$ composition ratios increase with increasing the plasma treatment time. This is clearly attributed to the increasing of oxygen groups on the carbon black surfaces increased as a function of the plasma treatment time. These results can be explained that the oxygen plasma treatment of the carbon black surfaces produces carbon radicals from the hydrocarbon backbone, followed by the formation of unstable hydroperoxides to produce various oxygen functional groups i.e., carboxyl, hydroxyl, lactone, and carbonyl groups, by reaction with additional oxygen.

3.2 MECHANICAL INTERFACIAL PROPERTIES

Fig. 2 shows the tearing energies measured in a trouser beam test. The results are revealed that the oxygen plasma treated carbon black filled-rubber composites are increased the tearing energy (G$_{mc}$) compare to as-received carbon black filled composites. And the tearing energy of the composites is increased with increasing the plasma treatment time. And the CB-20, which is higher acidic value and O$_{1s}$/C$_{1s}$ composition ratios component than the other samples, is higher tearing energy (G$_{mc}$) than those of rubber composites made from CB-5 and CB-10. It reveals that the polar rubber, such as, acrylonitrile butadiene rubber (NBR), shows a high degree of interaction with oxygen-containing functional groups of
the carbon black surfaces, resulting in improving the tearing energy ($G_{\text{MC}}$) of the carbon black/acrylonitrile butadiene rubber composites.

4. REFERENCES

3. X. Li and K. Horita, Carbon, 38, 133 (2000).

Table 1. Compounding formulations

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Loading [phr]</th>
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<tbody>
<tr>
<td>Rubber</td>
<td>100</td>
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<tr>
<td>Carbon black</td>
<td>40</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
</tr>
<tr>
<td>Dispersive agent</td>
<td>3</td>
</tr>
<tr>
<td>Accelerator</td>
<td>1</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2</td>
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</tbody>
</table>

*: Acrylonitrile butadiene rubber
b: N220
c: EF44
d: SCA 98
*: N-oxydiethylen-2-benzothiazole sulfenamide

Table 2. Results of pH and acid-base values of the carbon blacks studied.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>acid (meq/g)</th>
<th>base (meq/g)</th>
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<tbody>
<tr>
<td>CB-0</td>
<td>6.39</td>
<td>1200</td>
<td>300</td>
</tr>
<tr>
<td>CB-5</td>
<td>6.00</td>
<td>1500</td>
<td>400</td>
</tr>
<tr>
<td>CB-10</td>
<td>5.05</td>
<td>1900</td>
<td>700</td>
</tr>
<tr>
<td>CB-20</td>
<td>4.74</td>
<td>2200</td>
<td>700</td>
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</table>

Table 3. Results of the $O_{1s}/C_{1s}$ ratio of the carbon black studied.

<table>
<thead>
<tr>
<th></th>
<th>$O_{1s}/C_{1s}$ ratio [%]</th>
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<tbody>
<tr>
<td>CB-0</td>
<td>3.98</td>
</tr>
<tr>
<td>CB-5</td>
<td>4.19</td>
</tr>
<tr>
<td>CB-10</td>
<td>5.11</td>
</tr>
<tr>
<td>CB-20</td>
<td>5.31</td>
</tr>
</tbody>
</table>

*: specific surface area
b: BET's C
c: net heat of adsorption

Fig. 1 XPS survey scan spectrum of the carbon blacks studied.

Fig. 2 Tearing energy ($G_{\text{MC}}$) of the carbon black/rubber composites studied.