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Modifications produced by electrochemical treatments on carbon blacks
Microstructures and mechanical interfacial properties

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Abstract

In this work, the carbon blacks were electrochemically treated in an aqueous potassium hydroxide solution as a function of the electric current. As a result, this treatment led to a modification of the carbon surface properties, i.e., pH, acid–base values, anion exchanges, and microstructures. Especially, the electrochemical surface treatments appeared to be an increase of the basic surface functional groups and anion exchange properties with a consequence of a decrease in the interlayer spacing, d_{002} and an increase in the crystalline size along the *c*-axis, L_c, resulting in an improvement in the hardness and tearing energy of the carbon black–rubber composites. Also, it was found that a moderate basic surface treatment of carbon blacks seems a promising method of assessing the optimum improvement of physical or mechanical interfacial properties of composites. © 2001 Published by Elsevier Science Ltd.

Keywords: A. Carbon black; B. Electrochemical treatment; D. Interfacial properties; Microstructure; Surface properties

1. Introduction

Filled polymer systems are very popular for the composite industry for both cost and performance objectives. Carbon blacks are the most widely used reinforcing fillers, since they provide excellent reinforcement of general-purpose rubber at a relatively low cost [1].

The degree of interfacial adhesion in a composite system is of considerable importance. The load stress, transferred from the matrix to the reinforcement does require a strong adhesion at the interfaces between constituent elements [2–5]. Surface treatments of carbon materials have been generally used to improve the adhesive properties of carbon surfaces to a polymeric matrix, resulting in growing the final composite behaviors with a viewpoint of good mechanical properties and long durability [5–10]. Various methods used to modify the surface properties of the carbons are largely introduced in terms of gaseous oxidation, liquid phase oxidation, whiskerization, carbon or polymeric coating. Among them, the anodic liquid treatment appears to be one of the most flexible and promising liquid phase oxidation in the uniform and continuous processes in the carbon fiber manufacturing [9,11–17]. In this surface treatment system, a moderate oxidation of carbons is preferentially recommended for a real composite application, resulting in no significant change of the carbon surface aspects and in improving greatly the surface functional activity. Recently, Park et al. [18] proposed that the acidic anodic treatment on carbon fiber surfaces leads to an increase in the surface functional activity in the context of the acid–base interaction studies between acidified fibers and basic epoxy resin matrix, together with the results derived from the mechanical interfacial properties of a composite system.

Meanwhile, the interfacial adhesion of a solid depends largely on the surface energies, specific surface areas, active functional groups, energetically different crystallite faces, and so on [5]. Wang et al. [19] found that the change in the surface energy of carbon blacks is attributed to the growth of an organized microstructure. Obviously, more detailed investigations of the surface microstructure of carbon blacks are required in order to unveil the nature of the active centers and to improve the understanding of reinforcement by carbon blacks [20].

The aim of this work is to study the effect of basically

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anodized surface treatment on carbon blacks in increasing the surface functional activity and to understand the role of fillers on mechanical interfacial properties between nano-scaled carbon black and acidic elastomers in a composite system.

2. Experimental

2.1. Materials and sample preparation

Carbon blacks, (CBs, N 220 noted in ASTM destination) obtained from Korea Carbon Black Co., were used in this study. The carbon blacks were subjected to electrolytic reaction in an aqueous solution of potassium hydroxide (10 wt%), whereby negative ions were attracted to the surface of the carbon blacks acting as an anode, thereby modifying the carbon black surfaces. Electrolytic oxidation was performed in a batch system, where carbon blacks on the graphite bath filled with the electrolyte were fixed on a graphite anode roller. A cathode graphite plate was also submerged in the electrolyte solution. The conditions of the anodic oxidation are listed in Table 1. Prior to use following analysis, the residual chemicals used were removed by Soxhlet extraction with boiling with acetone at 80°C for 2 h. Finally, the carbon blacks were washed several times with distilled water and dried in a vacuum oven at 90°C for 12 h.

2.2. Surface and microstructure

The pH of the carbon blacks studied was measured according to ASTM D1512 based on the boiling and sonic slurry method. In this procedure, about 1 g of carbon black was added to 10 ml of freshly boiled distilled water. A few drops of pure acetone were used to facilitate wetting. The slurry was then heated until only the sludge remains. After the sludge cools to room temperature, its pH was measured with a glass pH electrode.

The acid–base values of the carbon black surfaces were determined by Boehm's method [21]. In the case of the acid value measurement, about 0.1 g of the sample were added to 100 ml of 0.1 N NaOH and shaking it for 24 h. Then, the solutions were filtered through membrane paper and titrated with 0.1 N HCl. Likewise, the base value was determined by the converse titration.

Table 1
Experimental conditions of the electrochemical surface treatments for carbon blacks

Conc. of electrolytes	10 wt% KOH
Temperature	20°C
Current intensities	0–5A
Oxidation time	30 min

The anion exchange capacity was determined by a dry weight capacity (DWC) technique [22]. The carbon blacks were converted into their Cl^- form by treatment with 0.1 M HCl solution and washed with distilled water. About 0.5 g of a sample was placed in 25 ml of distilled water in a beaker and 2 g of sodium nitrate ($NaNO_3$) for the anion exchange value (I_a). After 1 h of shaking at room temperature, the solution was titrated with 0.1 M $AgNO_3$ using a potassium chromate indicator for the anion exchange capacity.

Wide-angle x-ray diffraction (XRD) patterns of these samples were obtained with a Rigaku Model D/MAX-III B diffractometer equipped with a rotation anode and CuKα radiation (λ=0.15418 nm) as the source for measuring the interlayer spacing (d_{002}) and crystallite size along the *c*-axis (L_c).

2.3. Mechanical interfacial properties

In this work, the compounding formulations of the carbon black–rubber composites are reported in Table 2. For the measurement of the mechanical properties of filled vulcanizates, the compounds were cured under 1.5 MPa at 160°C for 60 min. Hardness measured by the Shore Durometer Hardness as type ''A-2'' on carbon black–rubber compounding according to the ASTM D2240.

The tearing energy (G_{IIIC}), which was one of the critical strain energy release rates (G_C), was characterized by trouser beam tests for mechanical behaviors of rubber compound composites [23]. Rectangular specimens with dimensions of about 100 mm long, 5 mm wide, and 5 mm thick were cut from a sheet that was manufactured by a two-roll mill technique. All tests were conducted at a crosshead displacement rate of 1 mm min^{-1}. Then, the tearing energy was calculated using the following equation [23–25]:

$$G_{IIIC} = \frac{2F}{t} \quad (1)$$

Table 2
Compounding formulations

Ingredients	Loading (phr)
Rubber[a]	100
Carbon black[b]	40
Zinc oxide	5
Stearic acid	2
Antioxidant[c]	1
Accelerator[d]	1
Sulfur	2

[a] Butadiene rubber.
[b] N220.
[c] 2,2,4-Trimethyl-1,2-dihydroquinone.
[d] *N*-Oxydiethylene-2-benzothiazole sulfenamide.