

# Preparation of Carbon Black/Natural Rubber Latex Masterbatch in Bead Form

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**ABSTRACT:** Carbon black/natural rubber latex masterbatch in the form of spherical beads was prepared according to the acid-precipitation method. High-loading carbon black (40 phr) was incorporated in natural rubber with the aid of a nonionic surfactant (Nonidet P40). Shearing the beads in an internal mixer provided good integration of carbon black in the rubber matrix and hence the high bound rubber content. Results confirmed the contribution of chemical interaction to the bound rubber content. By an oxidation process, the size of modified carbon black was reduced, whereas the large agglomeration took place in the case of partially graphitized carbon black. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 489–498, 2001

**Key words:** carbon black; natural rubber latex; masterbatch; bound rubber

## INTRODUCTION

It is well known that carbon black is an important reinforcing filler of rubber. Physical properties of the filled rubber depend mainly on the principal properties of carbon black such as particle size, surface area, aggregate structure and surface activity, its distribution in the rubber matrix, and rubber–filler interaction.<sup>1</sup> Thus the process of carbon black incorporation and dispersion is critically important. In general, an internal mixer or a two-roll mill is employed for mixing carbon black powder with solid rubber.<sup>1–5</sup> By using this technique, the high molecular weight rubber, particularly natural rubber (NR), is masticated, whereas carbon black agglomerates are broken down and dispersed in the masticated rubber under shearing and, thereby, rubber–filler interac-

tion takes place. However, such a conventional method not only consumes considerable amounts of energy and time to well disperse carbon black in rubber but other serious problems, such as loss of carbon black and its contamination in the factory, are also encountered.<sup>5</sup> Reports of works designed to bring the two main components together in such form that carbon black is incorporated in the rubber before compounding have appeared in the literature.<sup>1–5</sup> Both solid and latex forms of NR have been used for carbon black/rubber masterbatch preparation,<sup>3–9</sup> where it was found that compounding with latex could be processed with much less difficulty by producing the masterbatch in the form of loose, dry crumbs that were either compacted into bales or sheeted out.<sup>6–8</sup> Delivering the latex masterbatch to masticating equipment gave a shorter mixing cycle and provided a well-dispersed compound without noticeable loss of carbon black.<sup>5</sup>

Here, we report the preparation of carbon black/NR masterbatch in spherical bead form by using the acid-precipitation technique.<sup>10</sup> The advantage in having a product in bead form is that the task of cutting up the bales, to obtain the

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suitable weight rubber for convenient handling in further processing steps, is eliminated. Effects of mixing time in an internal mixer and extraction temperature on bound rubber content were investigated and carbon black was oxidized and partially graphitized to study the modified carbon black/NR interaction in the beads.

## EXPERIMENTAL

### Dispersion of Carbon Black in Nonionic Surfactant Solution

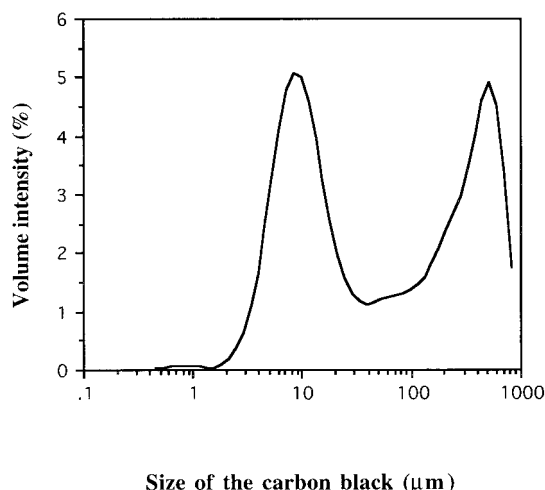
Carbon black powder Grade N220 (6 g), kindly provided by Thai Carbon Product Co., Ltd. (Chonburi, Thailand), was dispersed in various concentrations of aqueous solution of Nonidet P40 (25 mL; Fluka Chemie, Buchs, Switzerland) by ultrasonic process (Sonorex RK 100H, Berlin) for 15 min, after which solution samples were shaken (Burrell, Pittsburgh, PA) for 16 h at 25°C. The size of carbon black in 1–10% Nonidet P40 solutions [weight by weight of carbon black ( $w/w_{CB}$ )] was measured by using a laser particle size analyzer (Mastersizer S; Malvern, UK).

The carbon black dispersion was then centrifuged by a Supraspeed Centrifuge (Sorvall RC 28S; Dupont, Rockville, MD) at 15,000 rpm for 30 min. The supernatant layer was separated and repeatedly centrifuged before subjecting to UV absorbance (Spectronic Genesis 2; Spectronics, Westbury, NY) at 276.8 nm and surface tension (Tensiometer K8; Kruss GmbH, Germany) at 25°C measurements.

### Preparation of Carbon Black/Natural Rubber Bead

Carbon black powder [40 parts per hundred of rubber (phr)], dispersed in 1.5% ( $w/w_{CB}$ ) of Nonidet P40 aqueous solution, was mixed with concentrated high ammonia preserved NR latex having about 60% dry rubber content (DRC; Rayong Bangkok Rubber Co. Ltd, Rayong, Thailand). The mixture was then dropped via a capillary tube (3.6 mm in diameter) into a 90% aqueous acetic acid solution (100 mL; Merck, Darmstadt, Germany). The beads obtained were immersed in distilled water for 30 s to leach out acid before drying at 60°C. Dried beads (55 g) were then charged in an internal mixer (Haake Rheocord 90, Germany) at 50°C, rotor speed 50 rpm, for 4, 6, 8, or 10 min.

The morphology of the carbon black/NR sample, after being frozen in liquid nitrogen, cut by



**Figure 1** Size distribution of the carbon black powder dispersed in aqueous medium.

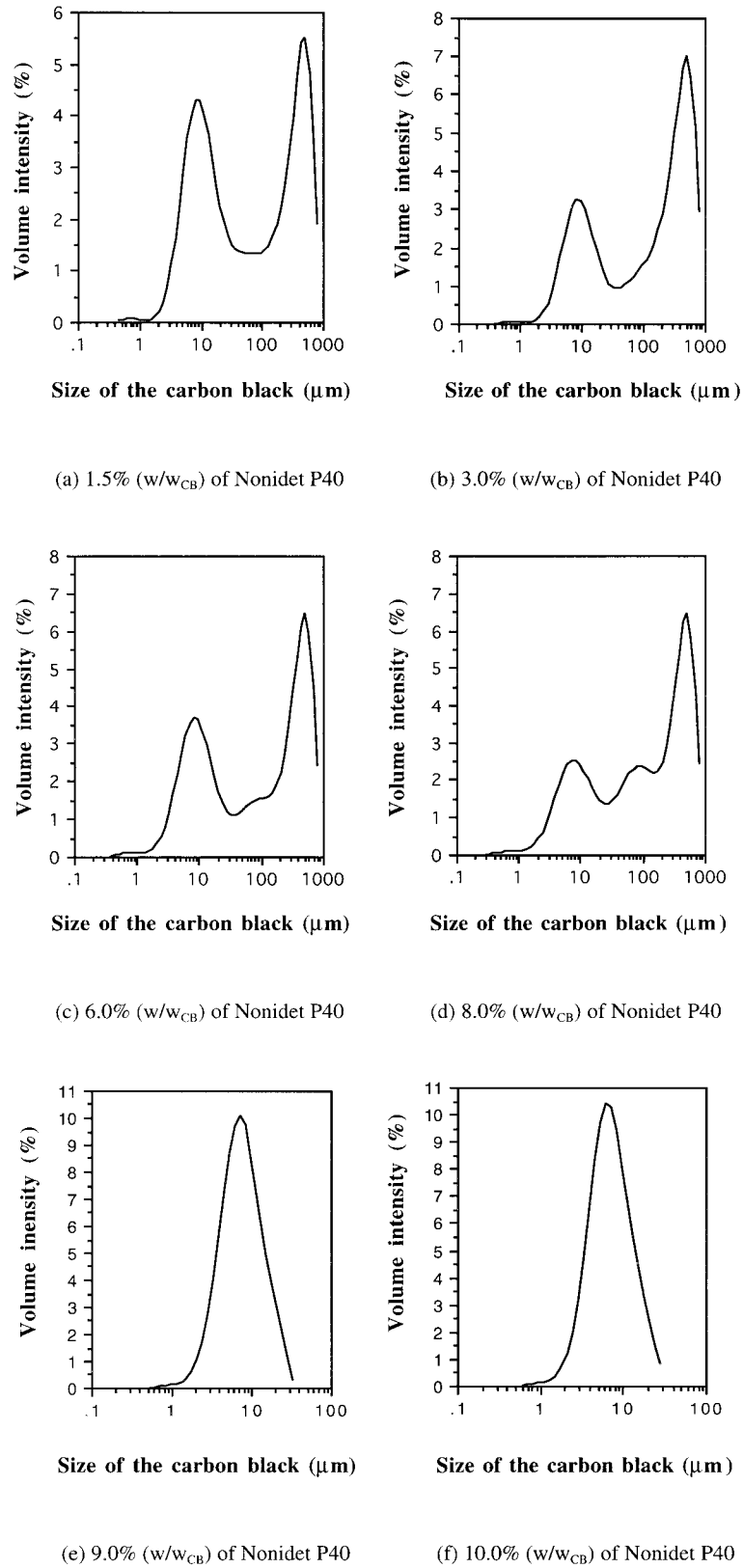
razor blade, and coated with Pt–Pd, was studied by scanning electron microscopy (SEM; Hitachi S-2500, Japan).

### Determination of Bound Rubber Content

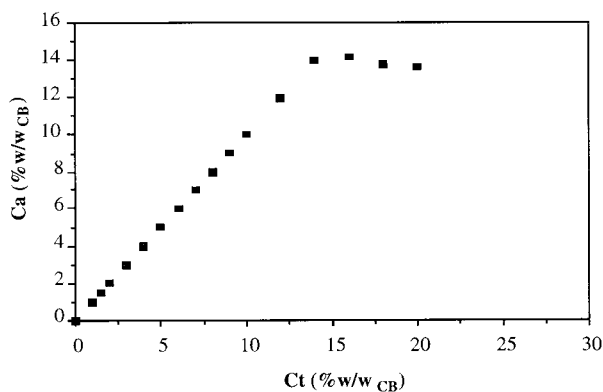
Bound rubber content ( $\%R_B$ ) was determined by extracting the carbon black/NR sample (0.3 g) with distilled toluene (200 mL; Fluka, commercial) according to the method previously described.<sup>11</sup> The extraction temperature was varied from 25 to 95°C. Continuous extraction using a Soxhlet extractor for 24 h was also applied.

### Modifications of Carbon Black

The carbon black was modified by liquid-phase oxidation and partial graphitization methods.<sup>11–13</sup> In the oxidation process, carbon black (50 g) was heated with 6M nitric acid (800 mL; Merck) to reflux for 3 h. The oxidized carbon black obtained was washed with distilled water until neutral and then dried at 120°C under vacuum for 24 h. In the partial graphitization process, the same amount of carbon black powder was placed in a tube furnace (Lenton Furnace, UK) at 1500°C for 3 h under nitrogen atmosphere. Constituents of the modified carbon black were characterized by elemental analysis (CHN Elemental Analyzer, 2400 CHN; Perkin Elmer Cetus, Norwalk, CT) and the size was measured before mixing with NR latex for bead preparation.



**Figure 2** Size distribution of carbon black dispersed in various concentrations of Nonidet P40 (% w/w<sub>CB</sub>): (a) 1.5%; (b) 3.0%; (c) 6.0%; (d) 8.0%; (e) 9.0%; and (f) 10.0%.



**Figure 3** Concentration of Nonidet P40 adsorbed on carbon black surface (Ca) against total concentration of Nonidet P40 initially added into the dispersion (Ct).

## RESULTS AND DISCUSSION

### Effect of Nonidet P40 on Size of Carbon Black

CHN elemental analysis of the carbon black N220 used in this study indicated the percentages of carbon, hydrogen, and nitrogen to be 95.7, 0.2, and 0.2%, respectively. Oxygen, therefore, constituted 3.9% of major elements. The carbon black powder was dispersed in distilled water for size determination, the results of which are presented in Figure 1.

It was observed that the carbon black in aqueous medium showed polydispersity in size, with a wide range of diameter varying from 1 to 800  $\mu\text{m}$ . The size distribution curve was bimodal, with the average particle diameters at 8.4 and 516.4  $\mu\text{m}$  ranging in agglomerate form.<sup>14</sup> Previous evidence showed that carbon black dust could not be dispersed in water without the assistance of either a wetting agent or steam grinding,<sup>5-9,15-18</sup> thus an aqueous solution of nonionic surfactant (Nonidet P40) was selected as a medium for dispersion. It was reasoned that the nonyl phenol group, a hydrophobic or anchoring part of the Nonidet P40 molecule, would be adsorbed on the hydrocarbon part of the carbon black surface, whereas the polyethylene glycol chain protruding in water would provide steric stabilization to the dispersed carbon black.<sup>16,18</sup> The effect of the surfactant concentration on the size of carbon black was investigated, the results of which are shown in Figure 2.

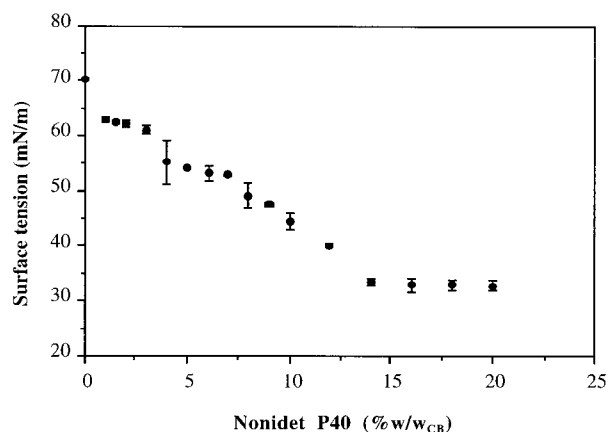
From Figure 2(a) and (b), it can be observed that the size distribution and average diameter of carbon black dispersed in low concentration of

aqueous solution of Nonidet P40 (1.5 or 3.0% w/w<sub>CB</sub>) were similar to those found in the surfactant-free carbon black shown in Figure 1. By increasing Nonidet P40 concentration to 6.0 and 8.0% (w/w<sub>CB</sub>), a small peak (88.9  $\mu\text{m}$ ) was additionally observed [Fig. 2(c) and (d)] and the size distribution became monomodal [Fig. 2(e) and (f)] when the surfactant concentration was 9.0 or 10.0% (w/w<sub>CB</sub>). A suggested explanation is that the amount of surfactant below 3.0% (w/w<sub>CB</sub>) was insufficient to completely cover the carbon black surface and the bridging effect might take place, that is, the surfactant molecule adsorbed on more than one carbon black particle, thus producing an aggregation.<sup>19-21</sup> However, the aggregation diminished at higher concentrations of Nonidet P40. A similar result was previously observed when polyisoprene sulfonate was used as the dispersing agent of carbon black.<sup>17</sup>

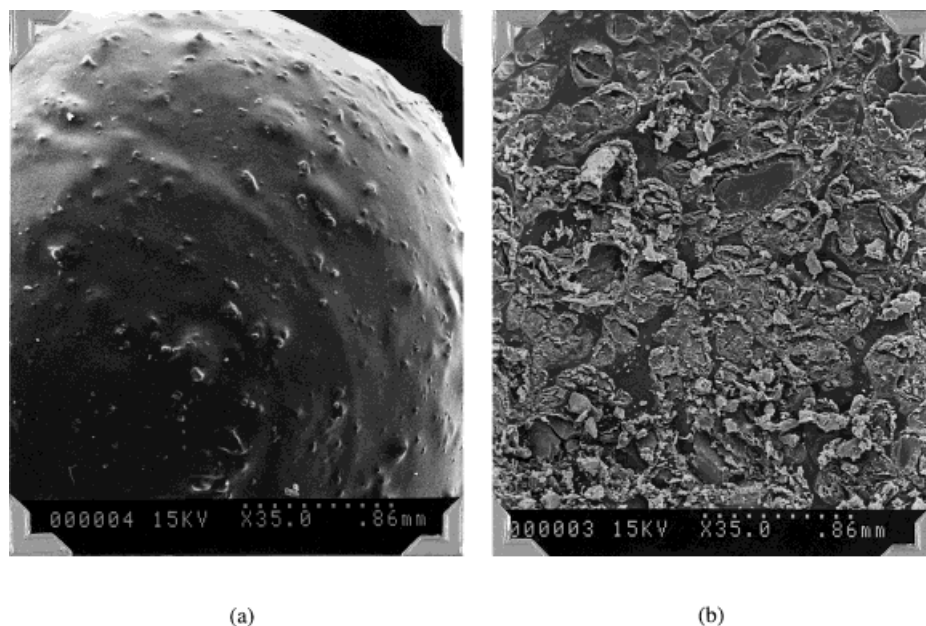
### Concentration of Nonidet P40 Adsorbed on Carbon Black

The amount of Nonidet P40 adsorbed on the carbon black surface (Ca) was calculated from the difference between the concentration of Nonidet P40 initially added into the dispersion (Ct) and the amount of surfactant left in the supernatant (Cs), as determined by the UV absorbance of each dispersion. The values of Ca obtained are plotted against Ct in Figure 3.

The data show that the concentration of Nonidet P40 adsorbed on the carbon black surface (Ca) linearly increased with the amount of added Nonidet P40 (Ct) from 0 to 14% (w/w<sub>CB</sub>). The



**Figure 4** Surface tension of supernatant solution of the carbon black dispersed in various concentrations of aqueous solution of Nonidet P40.



**Figure 5** SEM micrographs ( $\times 35$ ) of carbon black/natural rubber bead (a) surface and (b) cross section.

latter thus represented the maximum concentration of Nonidet P40 completely adsorbed on the carbon black surface. This concentration was also measured as a minimum value of the surfactant, initially providing constant surface tension of the supernatant, as presented in Figure 4.

#### Morphology of Carbon Black/Natural Rubber Bead

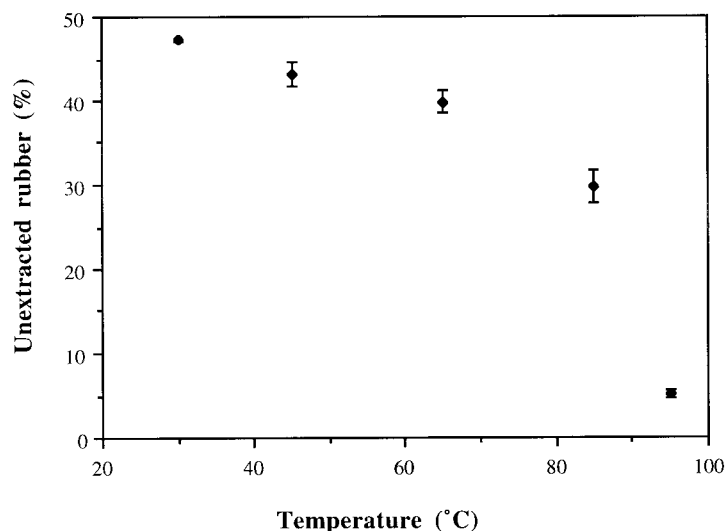
When carbon black, dispersed in less than 1.5% (w/w<sub>CB</sub>) of aqueous solution of Nonidet P40, was gently mixed with concentrated NR latex, coagulation was visually observed. The result indicated that 1.5% (w/w<sub>CB</sub>) Nonidet P40 was sufficient to provide steric stabilization or to prevent coagulation of the carbon black and NR particles. At this concentration the size distribution of carbon black in aqueous medium remained unchanged, as previously shown in Figure 2(a), and surfactant molecules incompletely covered the carbon black surface, as observed in Figures 3 and 4. When the mixture of carbon black dispersion and NR latex was dropped into a solution of 90% aqueous acetic acid, spherical beads of 4.5 mm diameter were obtained. Morphologies of the surface and cross section of the dried beads under SEM are displayed in Figure 5.

The micrograph shown in Figure 5(a) reveals the presence of only a small amount of carbon black on the bead surface, that is, the majority of

carbon black could be embedded into the NR bead matrix. This points to the remaining nonpolar character of the carbon black surface, even after dispersing in 1.5% (w/w<sub>CB</sub>) of Nonidet P40 solution. It was also observed in Figure 5(b) that carbon black was well dispersed within the bead in the form of agglomerate, which was not suitable for reinforcing rubber.<sup>14,22</sup>

#### Effect of Extraction Temperature on Bound Rubber

Amounts of the unextracted rubber portion in the carbon black/NR and carbon black-free NR beads determined at 25°C were  $43.9 \pm 0.8$  and  $43.1 \pm 0.7\%$ , respectively. These values correlate well with the gel content of NR previously reported,<sup>23,24</sup> which implied that the figures might not be bound rubber content as normally detected in other works.<sup>25–28</sup> Thus the Soxhlet method was applied in the extraction of the beads and it was found that the percentages of unextracted NR of the unfilled and filled NR were  $0.9 \pm 0.4$  and  $0.5 \pm 0.3$ , respectively. The very low unextracted NR possibly resulted from the gel breakage in the rubber.<sup>25,29</sup> The effect of extraction temperature was further studied by extracting the carbon black/NR beads with toluene at various temperatures and the percentages of unextracted NR obtained are presented in Figure 6. It was observed that the amount of unextracted NR slowly de-



**Figure 6** Effect of extraction temperature on unextracted NR of carbon black/natural rubber beads.

creased with increasing temperature and then abruptly decreased at 65°C, that is, the gel of NR might be slightly damaged at low temperature and almost totally destroyed at high extraction temperatures.

#### Effect of Shearing

Because the experiment showed only the gel formation in the carbon black/NR bead, the beads were subsequently mixed in an internal mixer to generate bound rubber by shearing. The mixing time was varied and the percentage of unextracted NR from each experiment was determined by extraction of the sheared beads with toluene at 25°C. Data obtained are shown in Table I, which indicates a significant increase of the amount of

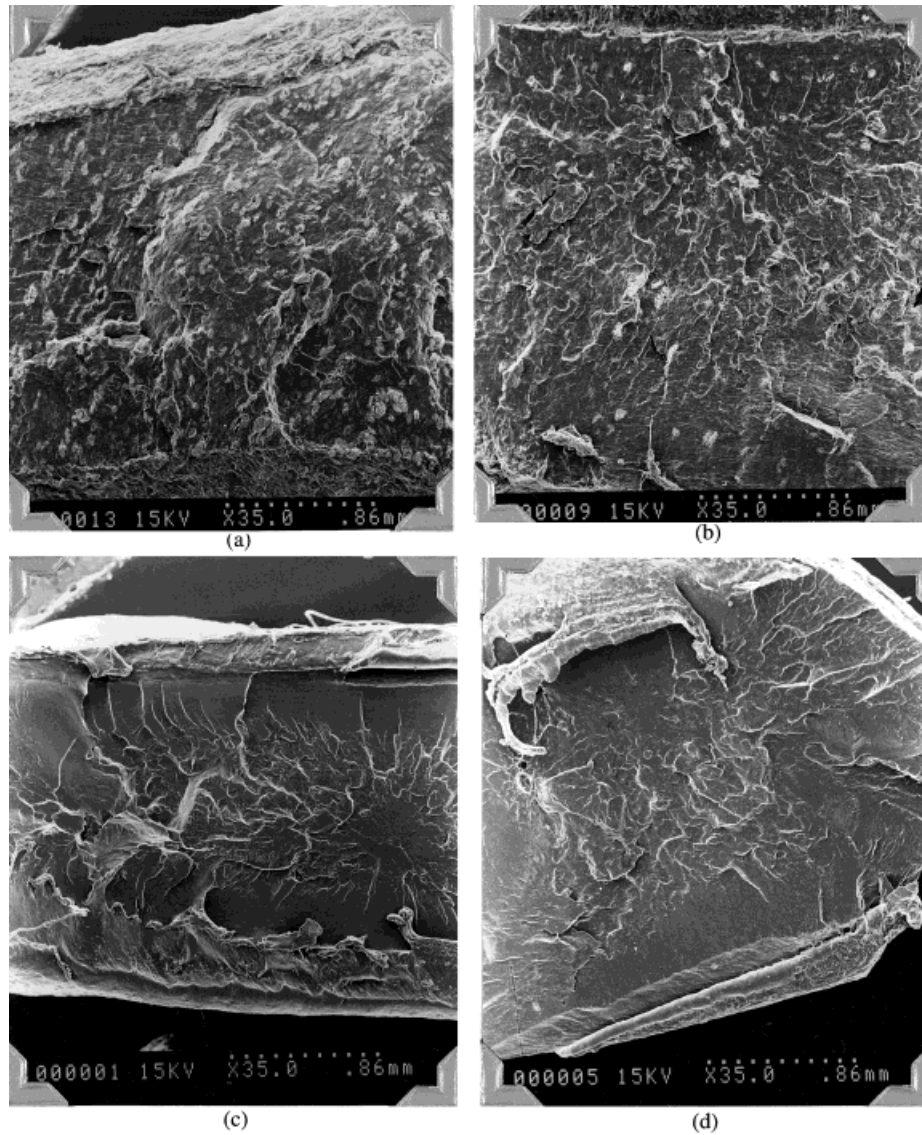
remaining NR attached to carbon black when the mixing time was prolonged from 4 to 10 min. The applied shear force enhanced the carbon black/NR interaction, probably by reducing the size of carbon black and, hence, increasing its surface area.<sup>22,30,31</sup> It was noticed that the percentage of unextracted NR (at 25°C) of sample mixed within 4 to 8 min was low when compared to that of carbon black/NR bead. The same amount of the remaining NR was observed when the mixing time was 10 min, indicating that the shear force could simultaneously generate carbon black/NR interaction and break the gel of NR molecules.

As already stated, physical interaction normally broke out with the increase extraction temperature; thus, the samples after shearing were then extracted by using the Soxhlet method and results are also shown in Table I. In this case the quantity of unextracted rubber was greater than that in the beads prior to shearing, implying the existence of chemical interaction between carbon black and NR in the sheared sample. Under shear force, chain scission of NR molecules, resulting in the formation of free radicals, might take place<sup>1-3,11</sup> and the radicals subsequently reacted with the active sites (e.g., carboxyl, lactone, phenol, and quinone) on the carbon black surface to form the bound rubber. Prolonging of the mixing time resulted in a greater amount of free radicals on NR chains, which caused higher bound rubber content.

**Table I** Unextracted NR of Unfilled and Filled Rubber After Shearing the Beads in Internal Mixer at Various Mixing Times<sup>a</sup>

Mixing Time (min)	Unextracted NR (%)	
	Extraction at 25°C	Soxhlet Method
0	43.1 ± 0.7	0.5 ± 0.3
4	19.4 ± 1.0	1.6 ± 0.3
6	26.2 ± 0.4	8.0 ± 0.4
8	36.5 ± 0.4	15.7 ± 1.3
10	45.1 ± 1.4	23.1 ± 1.9

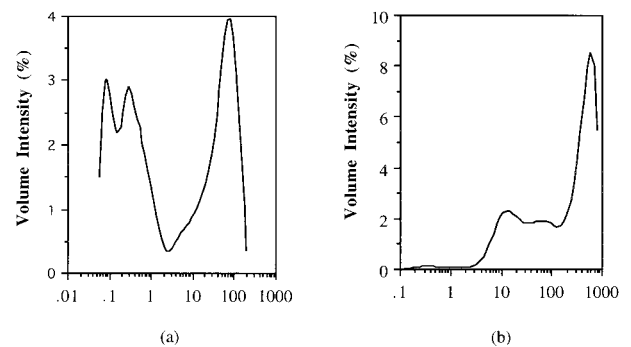
<sup>a</sup> Extraction with toluene at 25°C and using the Soxhlet method.



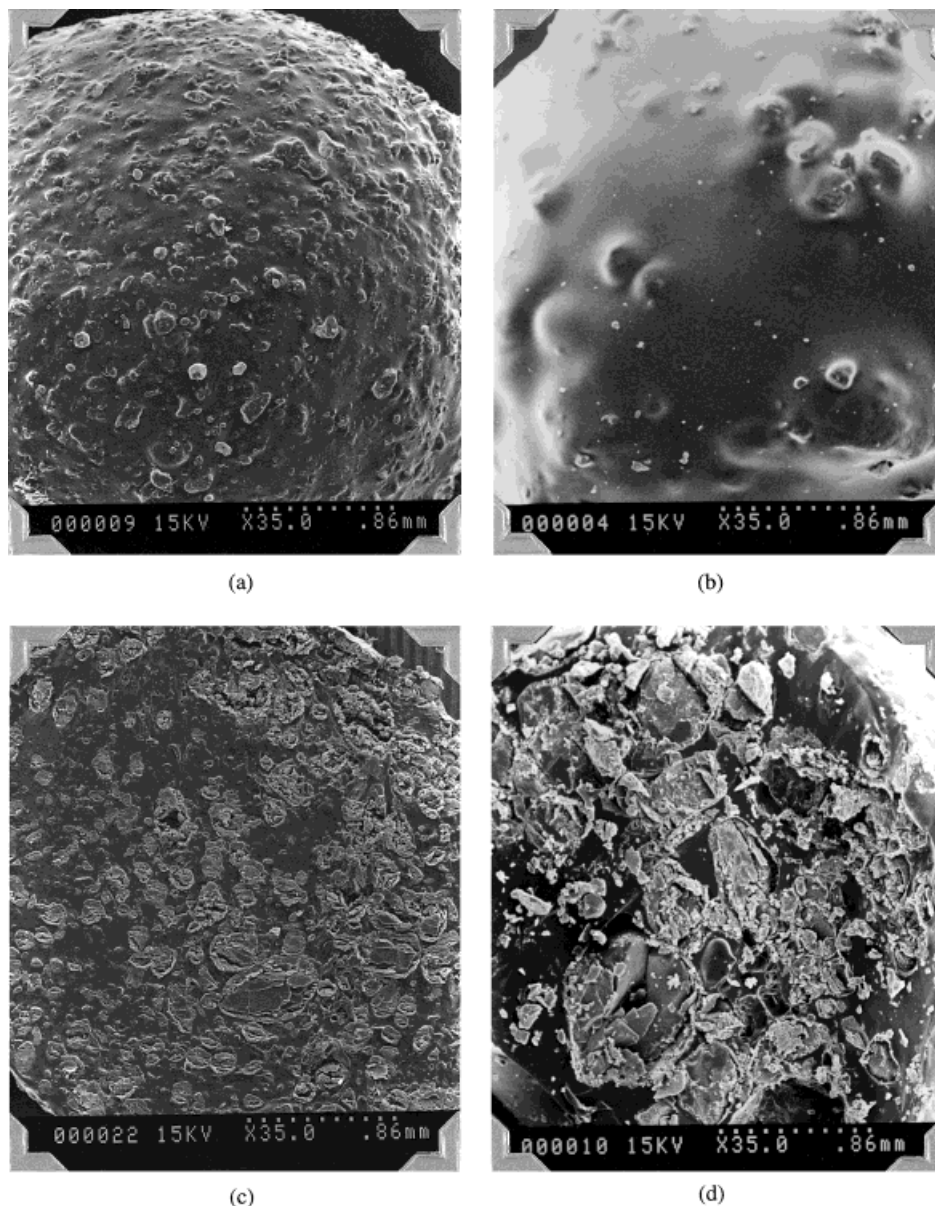
**Figure 7** SEM micrographs of cross section ( $\times 35$ ) of samples after shearing carbon black/natural rubber beads in internal mixer at: (a) 4 min, (b) 6 min, (c) 8 min, and (d) 10 min.

**Table II** Percentage of Elements of Unmodified, Oxidized, and Partially Graphitized Carbon Black

Element	Unmodified Carbon Black (%)	Oxidized Carbon Black (%)	Partially Graphitized Carbon Black (%)
C	95.7	87.9	97.9
H	0.2	0.5	—
N	0.2	0.3	0.3
O	3.9	11.3	1.8



**Figure 8** Size distribution curves of (a) oxidized and (b) partially graphitized carbon black in aqueous medium.



**Figure 9** SEM micrographs ( $\times 35$ ) of modified carbon black/natural rubber beads: (a) oxidized carbon black/NR surface, (b) partially graphitized carbon black/NR surface, (c) oxidized carbon black/NR cross section, and (d) partially graphitized carbon black/NR cross section.

The change in size of carbon black in samples at various mixing times was investigated under SEM as shown in Figure 7. The micrographs indicate that the size of carbon black in the product after shearing was much smaller than that in the carbon black/NR bead [Fig. 5(b)] and the presence of carbon black could not clearly be noticed under the longer mixing time [Fig. 7(c) and (d)], indicating good integration of carbon black in NR.

#### Modified Carbon Black/Natural Rubber Bead

To study the interaction between carbon black and NR in the beads, the carbon black was modified by using two methods, that is, liquid-phase oxidation and partial graphitization before mixing with NR latex for bead preparation. The percentage of elements of the modified carbon black, as determined by CHN Elemental Analyzer, are presented in Table II.



It is noted that the oxygen content in the carbon black increased by the oxidation process and decreased by partial graphitization. Determination of the quantity of carboxyl groups in the oxidized carbon black by using the titration method<sup>32</sup> was found to be  $2.5 \times 10^{-3}$  (mol/g of carbon black), which was higher than that in the unmodified carbon black ( $1 \times 10^{-5}$ ). The data agreed well with the previous report that the basic pH (8.3) of unmodified carbon black changed to an acidic pH (2.7) after oxidation.<sup>11</sup>

Sizes of oxidized and partially graphitized carbon black in aqueous medium were then measured and their distribution curves are shown in Figure 8(a) and (b), from which it is observed that both curves exhibit multimodal type and the size of unmodified carbon black (Fig. 1) was greater than that of the oxidized carbon black [Fig. 8(a)] but smaller than that of the partially graphitized carbon black [Fig. 8(b)]. This phenomenon could be explained in terms of the increase in repulsion between the particles caused by the greater polarity produced by functional groups presented on the oxidized carbon black surface. By the same analogy, it could be assumed that the agglomeration took place in the case of partially graphitized carbon black.

Modified carbon black/NR beads were also prepared and their morphologies under SEM are presented in Figure 9. A considerable amount of small agglomerate oxidized carbon black on the bead surface was revealed in Figure 9(a), whereas the presence of a small amount of carbon black with large agglomerate size on partially graphitized carbon black/NR bead surface was observed in Figure 9(b). The micrographs implied that the blend oxidized carbon black with the nonpolar rubber was less miscible in the matrix than in the case of low polar partially graphitized carbon black. The small size of agglomerate oxidized carbon black [Fig. 9(c)] and the large partially graphitized carbon black in the beads [Fig. 9(d)] apparently resulted from the repulsion between functional groups on the modified carbon black surface, as previously mentioned.

The values of the unextracted NR obtained from extraction of the beads containing partially graphitized carbon black at 25°C and the Soxhlet method were, respectively, 45.6 and 1.5%, which were similar to those of the unmodified carbon black/NR and of unfilled NR beads as presented in Table I. The results indicated that the incorporation of partially graphitized carbon black in beads did not improve the interaction (or bound

rubber) of modified carbon black/NR because of its large agglomerate size and crystalline structure, leading to the loss of active sites.<sup>3,13</sup> Unfortunately, the percentage of unextracted NR in oxidized carbon black/NR beads could not be accurately measured in our experiments because the oxidized carbon black and NR were coextracted into toluene at all extraction temperatures in our study.

## CONCLUSIONS

Study of the preparation of carbon black/NR latex masterbatch in bead form led to the following conclusions. First, the amount of surfactant (Nonidet P40) used affected the size distribution of carbon black slurry and coagulation of the carbon black dispersion mixed with NR latex. Second, carbon black agglomerates (40 phr) could be incorporated in the bead matrix, forming about 43% of gel content. Third, the bound rubber was formed when the beads were sheared in the internal mixer. Prolonging of the mixing time caused higher bound rubber content. Finally, the blend oxidized carbon black containing higher polar functional group with NR was less miscible in the bead matrix than in partially graphitized/NR.

By reason of its convenient form to handle, compounding with the bead masterbatch is now under investigation in our laboratory and results will be presented in future reports.

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