Study on properties of natural rubber reinforced by poly(sodium-4-styrenesulfonate)-decorated carbon black with a latex compounding technique

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ABSTRACT: Natural rubber filled with poly(sodium-4-styrenesulfonate) (PSS)-decorated carbon black (CB) by employing a latex compounding technique was prepared. The result of scanning electron microscope demonstrated that CB was uniformly dispersed in the matrix. Comparing to traditional dry compounding, an improvement in physical and mechanical properties was observed in the composites attributed to the homogeneous distribution of CB in matrix and an augment of bound rubber. Owing to the changes of the physical properties of CB surface, vulcanizate filled with oxidized CB via latex way exhibited higher mechanical properties. The resulting vulcanizates displayed a diminished interaction between fillers based on the consequence of strain dependence of storage modulus. Furthermore, a splendid wet-skid resistance was obtained in vulcanizates fabricated by latex compounding technique in comparison with vulcanizates prepared by traditional dry compounding. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42346.

INTRODUCTION

Carbon black (CB) is one of the most important filler in the industry of rubber since it can remarkably improve the properties of the matrix. The introduction of CB can often enhance the tensile strength and tear resistance of the filled composite. It is well recognized that the particle size, structure, surface activity of CB have large influence on the physical performance of elastomeric materials.[1] Moreover, the dispersion of CB in the matrix is also an important factor to the result of reinforcement.[2] However, CB particles are difficult to disperse into matrix attributed to their small primary particle size (about 20–60 nm), which means they are prone to form aggregates.[3] These aggregates are readily held together by Van der Waals' forces to form agglomerates and are difficult to break up,[4] and in turn, weaken the properties of the material.[5] Deterioration of tensile strength, dynamic fatigue and hysteresis properties can be often observed when CB is nonuniformly dispersed in the composite. In order to weaken the aggregation of CB particles and make it reach a homogeneous dispersion in the matrix, great efforts have been made.[6,7]

In the past two decades, latex compounding technique, which means the filler is dispersed into rubber latex instead of solid mixing, has attracted researcher's great attention.[8–14] However,

studies about CB in this field received much less concern ascribed to its strong hydrophobicity different with other fillers such as silicon dioxide and magnesium hydroxide. As a good hydrophilicity is required in its application fields, preparing stable dispersions of CB in aqueous medium by a low cost, technically straightforward and environment-friendly method is of great importance and in urgent needs. Until now, several methods have been developed to improve the hydrophilicity of CB in aqueous medium, such as oxide treatment,[15–18] graft modification,[19–24] and surface coating,[25–28] etc. Oxidation reaction could not provide CB excellent dispersity in water ascribed to the limited carboxyl group and hydroxyl group on the surface of CB. Meanwhile, graft modification involves complicated polymerization and requires harsh conditions, such as high temperature, anaerobic environment while the grafting ratio enhances little. All these drawbacks restrict their application in the industry.

In our previous research,[29] we successfully prepared poly(sodium-4-styrenesulfonate) (PSS)-decorated hydrophilic CB via *in situ* peeling of large CB aggregates into small pieces. The obtained PSS-decorated CB displayed an outstanding stability in water through strong π–π interactions. In this paper, we focused on the properties of natural rubber reinforced by this kind of hydrophilic CB with a latex compounding technique. The morphology of modified CB nanoclusters in rubber matrix was

observed by scanning electron microscope, and the mechanical properties and dynamic mechanical properties of the resulting vulcanizates were investigated. In addition, the influence of oxidation treatment of CB on properties of this kind of nanocomposites was also discussed.

EXPERIMENTAL

Materials

A commercial medium ultra abrasion furnace black (N234, obtained from Cabot) with a mean diameter of about 20–25 nm was chosen for this study. These CB particles were dried for 24 h at 105°C under vacuum before use. Poly(sodium-4-styrenesulfonate) (PSS) solution with a solid content of 20 wt % was purchased from Shanghai Herochem, while hydrogen peroxide (H_2O_2) was obtained from Shanghai Lingfeng Chemical Reagent. Natural rubber latex (NRL) (solid content: 61 wt %) was kindly provided by Tech Bee Hang Corp.

Oxidation of CB

Oxidation treatment was carried out by refluxing 80 g CB with 700 mL hydrogen peroxide solution in a three-necked round-bottom flask with a 300 rpm stirring rate at 100°C for 24 h. The oxidized CB (CBO) was filtered, washed with deionized water several times, and finally dried under vacuum at 80°C for 24 h.

Preparation of PSS-Decorated CB/CBO

25 g CB or CBO, 12.5 g PSS solution, 250 g deionized water and the grinding balls were put in a grinding bowl, and then the bowl was placed into a planetary ball milling (QM-1SP2, Nanjing University instrument plant). After 12 h treatment, PSS-decorated CB/CBO dispersed in water was obtained.

Preparation of Hydrophilic CB Filled Natural Rubber by Latex Compounding Technique

Firstly, pH value of PSS-decorated CB/CBO dispersion and NR latex with a total solid content of 20 wt % (it had been diluted before use) was adjusted to 10.0 with 0.2M NaOH. Then, the PSS-decorated CB/CBO aqueous dispersion was added into NRL drop by drop under mechanical stirring at room temperature. After another 30 min stirring, the dispersion was precipitated by $CaCl_2$ aqueous solution (10 wt %). Finally, the obtained precipitation was dried overnight at 70°C under vacuum until the weight remained constant.

The dispersion of other ingredients was achieved by blending them on an open mill at 50°C with a friction ratio of 1.2 : 1 in the following proportions: ZnO 2.0 parts per hundred rubber (phr); stearic acid 4.0 phr; sulfur 1.2 phr; accelerator M 2.0 phr. The vulcanization was carried out in all cases in a press of 100 MPa at 140°C in an optimum cure time determined by MDR 2000 (Wuxi Liyuan, China). To simplify the following discussion, vulcanizates filled with PSS-decorated CB and CBO via latex compounding technique were abbreviated as W-CB and W-CBO, respectively.

Traditional blending of CB and NR which is known as dry compounding was performed on the open mill at 50°C. The formula and vulcanization process were same as W-CB and W-CBO. The obtained product was abbreviated as D-CB.

Characterization

The distribution of CB in NR vulcanizate was investigated by scanning electron microscope (SEM) (S-3400N, Hitachi) at an acceleration voltage of 10 kV. The fracture surface was obtained by splitting bulk sample in liquid nitrogen and the samples were coated with a thin layer of gold before observation.

Physical and mechanical properties including tensile test (GB/T 528–1998) and tear resistance (GB/T 529–1999) experiments were carried out on an Instron Series IX Automated Materials Testing System (Acton, MA) with a crosshead speed of 500 mm/min under room temperature.

Bound rubber (BR) content was measured by immersing 0.5 g unvulcanized rubber compound (1 week after mixing) wrapped by filter paper in 100 mL methylbenzene for 8 days under room temperature. The methylbenzene was replaced every 2 days. 8 days later, the rubber compound was moved into 100 mL acetone for another 2 days immersion. In the end, the rubber compound was dried overnight at 70°C under vacuum until the weight remained constant.

The specific surface area and pore volume were measured by low-temperature nitrogen adsorption method (BET method) on Surface Area and Porosimetry System (ASAP 2010N, Michael Instruments Company).

Strain dependence of storage modulus was measured using a rubber processing analyzer (RPA2000, Alpha) under a constant frequency of 11 Hz at a temperature of 20°C.

The temperature dependence of dynamic mechanical properties was measured via a dynamic mechanical analyzer (UBM Rheogel E4000, Japan) and the measurements were completed under a constant frequency of 11 Hz, a heating rate of 5°C/min and a temperature range from −80 to 80°C.

RESULTS AND DISCUSSION

Mechanical Properties of Natural Rubber Reinforced by Hydrophilic CB

Figure 1 shows the tensile strength of W-CB and D-CB at different loading of CB. Compared to D-CB, W-CB displayed an outstanding tensile performance according to Figure 1. The tensile strength of W-CB vulcanizate increased to 21.7 Mpa at a loading level of 40 phr while that of D-CB was 17.9 Mpa (tensile strength of neat natural rubber was only 9.7 Mpa), which means an enhancement of 21% was achieved. The increase in tensile strength imparted by PSS-decorated CB is reasonably well understood. Unlike D-CB, the blending process of CB and natural rubber was completed in aqueous medium during fabricating W-CB. When the modified CB which is highly hydrophilic was added into NR latex, the resulting mixture can reach to a nanoscale distribution after stirring. That is to say, CB can be dispersed in matrix uniformly after precipitation and vulcanization; therefore, less stress concentration would be formed, finally leading to the improvement of tensile strength. The SEM result shown in Figure 2 demonstrated it. In the SEM photo of D-CB composite, a quite broad distribution of the particle size and large aggregates were observed clearly. Whereas in the SEM photo of NRL/PSS decorated-CB composites (W-CB and W-
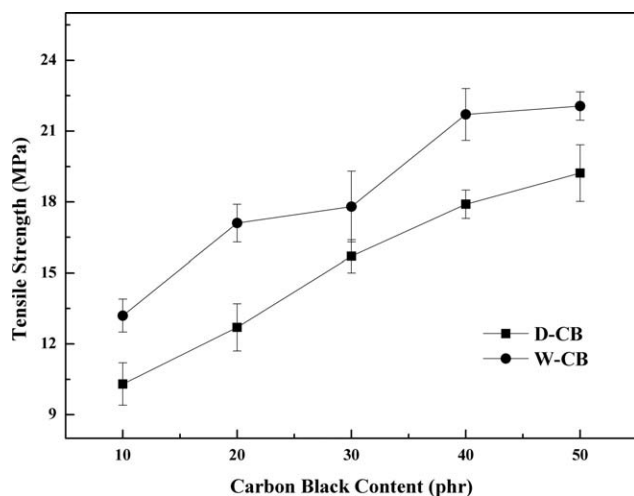
Figure 1. Tensile strength of D-CB and W-CB at different loading of carbon black.

$$m = \frac{m_2 - m_1 \times \omega_2}{m_1 \times \omega_1} \tag{1}$$

where m was the bound rubber (BR) content (g/g), m_1 and m_2 were the weight of rubber compound before and after immersion, ω_1, ω_2 were mass fraction of rubber and CB in the composite, respectively. The BR content of unvulcanized W-CB and D-CB at different loading of CB was shown in Figure 5. It can be observed that the bound rubber content of W-CB exhibited a distinct increase in comparison with D-CB, indicating a
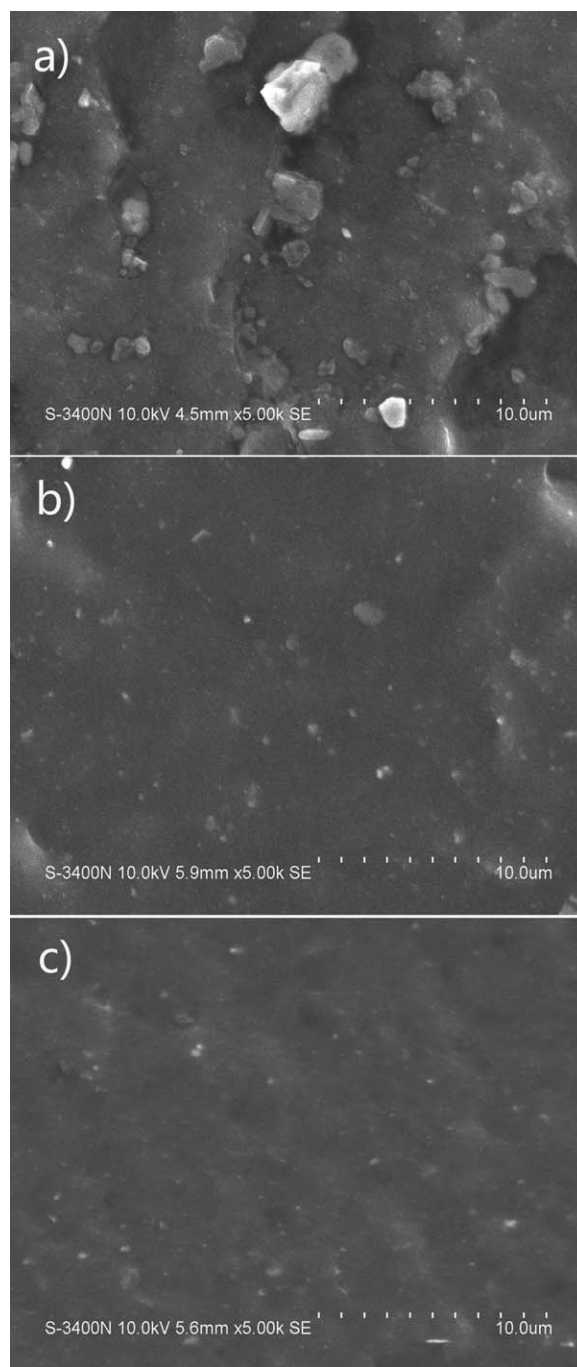
CBO), CB was uniformly dispersed in the matrix that no obvious aggregation was discovered, and the domain size of dispersed phase is remarkably decreased. The elongation at break of W-CB and D-CB at different loading of CB was shown in Figure 3. As shown in Figure 3, the elongation at break of W-CB was much greater than that of D-CB. This kind of increase could be reasonable, as this property reacts very sensitively on impurities in the material like big CB agglomerates. According to the SEM photograph, a mass of CB agglomerates were observed in the D-CB material, which means the movement of polymer chains would be restrained when subjected to stress, leading to a decrease of elongation at break.

CB can considerably enhance the tear strength of rubber product via the stress dissipation at the tip of a growing crack by a viscoelastic process. Figure 4 shows the tear strength of W-CB and D-CB vulcanizates at different loading of CB. It can be seen from Figure 4 that W-CB displayed an extraordinary tear property in comparison with the product prepared by dry compounding. The tear strength of W-CB at 40 phr loading of CB was 68.3 kN/m while that of D-CB was only 29.9 kN/m (tear strength of neat natural rubber was only 13.2 kN/m), which means the tear strength was increased by 128%. For W-CB, the dispersion of CB in the matrix was improved when employing latex compounding technique instead of dry blending, which has been proved by SEM. Less stress concentration was formed and thus an enhancement of tear strength was achieved.

Furthermore, the filler–polymer interaction characterized by bound rubber content was another significant influence condition to the reinforcement result.[30] The strong interfacial interaction of reinforcing CB and rubber molecule chains promoted further dissipation of the applied stress by means of increased hysteresis, and thereby much higher resistance to tearing was achieved. In the present study, the enhancement of mechanical properties of W-CB especially the tear strength should be attributed to the increase of filler–polymer interaction. The bound rubber can be calculated by the following formula:

Figure 2. SEM micrographs of (a) D-CB, (b) W-CB, (c) W-CBO at a carbon black content of 40 phr.

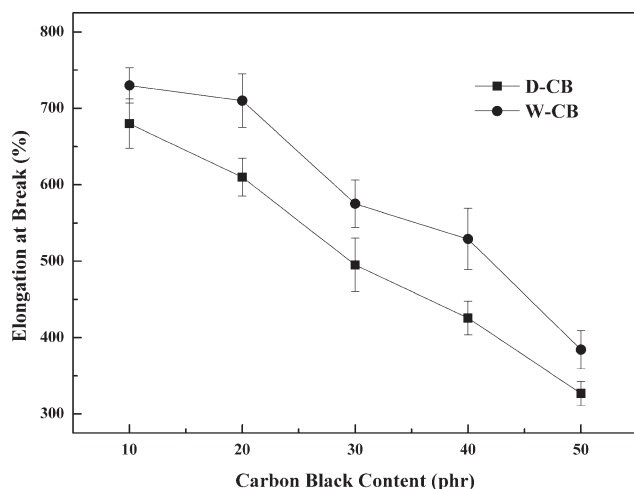**Figure 3.** Elongation at break of D-CB and W-CB at different loading of carbon black.

Figure 5. Bound rubber content of D-CB and W-CB at different loading of carbon black.

stronger filler–polymer interaction was formed in W-CB. It might be because that the PSS chains adsorbed on the decorated CB via a physical interaction would desorb when the mixture of CB and NR was subjected to a shear force on the open mill under a temperature of 50°C. At the same time, NR molecule rapidly occupied the fresh surface and formed bound rubber with the active site on it. Much more contact surfaces would be exposed in W-CB ascribed to the outstanding distribution of CB in the matrix, leading to an increase of BR content. Whereas the specific surface area of CB in D-CB vulcanizates was relatively smaller because of its aggregation, and the decrease of contact opportunity between NR molecule and CB surface finally resulted in a subdued interaction.

Figure 6 shows the mechanical properties and BR content of D-CB, W-uCB (systems with unmodified CB prepared via latex way), D-PCB (systems with PSS-modified CB prepared by dry compounding), W-CB, W-CBO, and D-CBO (systems with CBO prepared by dry compounding) when the filling content of CB was 40 phr. A decline in mechanical properties of
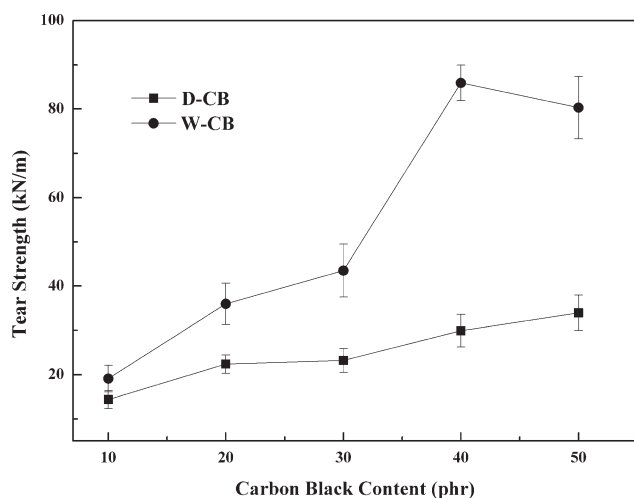
W-uCB was clearly observed in comparison with D-CB and W-CB. It was because that the unmodified CB was strong hydrophobicity as we discussed before, which resulted in a deterioration of the disperse state of CB when mixed with latex. And the dried precipitation was immediately mixed with other ingredients on an open mill without a particular time for the dispersion of CB, which means that its mixing time was much shorter than D-CB. Comparing to D-CB and W-CB, the tensile strength and tear strength of D-PCB was in between. It can be ascribed to the PSS chains adsorbed on the surface of CB, which restrained the aggregation between the particles. But the latex way can provide better dispersion of CB in the matrix, the mechanical properties of D-PCB could not surpass W-CB. In addition, higher BR content was observed in W-CBO, which resulted in a better mechanical property than that of W-CB. It could be attributed to the changes of the physical properties of CB surface after oxidation treatment (results were listed in Table I). As we can see from Table I, the specific surface area increased from 110.3 to 113.8 m^2/g and the change of internal surface area was 32% (from 15.8 to 20.8 m^2/g) among the

Figure 4. Tear strength of D-CB and W-CB at different loading of carbon black.
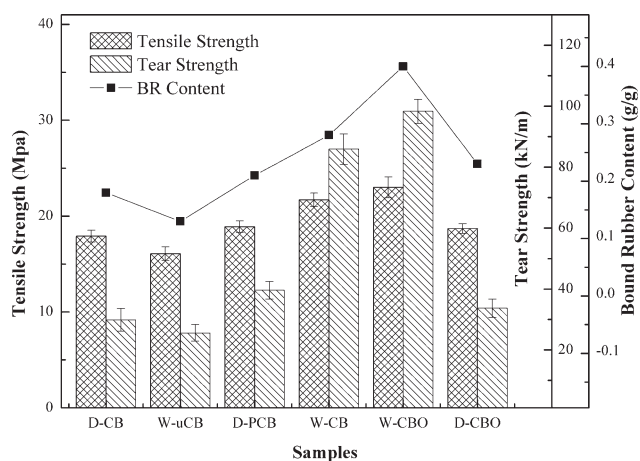

Figure 6. Mechanical properties and BR content of D-CB, W-uCB, D-PCB, W-CB, W-CBO and D-CBO (40 phr).

Table I. BET Surface Area, Pore Volume, and Pore Size of CB and CBO

| Sample | BET surface area (m^2/g) | | | Pore volume (cm^3/g) | Pore size (nm) |
	Internal	External	Total		
CB	15.8	94.5	110.3	0.72	26.06
CBO	20.8	93.0	113.8	0.81	26.54

enhancement of specific surface area while the pore volume increased 12.5%, which means the surface roughness of CB was increased.[31] The enhancement of specific surface area could create more contact opportunity between CBO and NR molecule while the increase of surface roughness could intensify the adsorption of polymer chains on the surface of CB, which finally leading to an improvement of mechanical properties.

Strain Dependence of Storage Modulus

It is well known that when filled with CB, rubbers show typical nonlinear viscoelastic behavior during dynamic deformation, namely storage modulus (G') decreased from G_0 to a high amplitude plateau value G_J with the increase of deformation, which was called Payne effect.[32,33] Payne put forward that the storage modulus of the filled vulcanizate depended on polymer network, hydrodynamic effects. In rubber structure (interaction between filler and rubber) and the filler–filler interaction when subjected to a dynamic strain. The first three had nothing to do with deformation; however the last one was on the contrary. This phenomenon was interpreted as a result of the breakage and reestablishment of interaction between filler aggregates. Figure 7 shows the strain dependence of storage modulus for D-CB, W-CB, and W-CBO vulcanizates. It can be seen that storage modulus of all filled rubber diminished with the increase of deformation, showing a typical nonlinear behavior. However, higher storage modulus was observed in D-CB vulcanizate in comparison with W-CB and W-CBO while their storage modulus under high strain was nearly the same, which indicated that the aggregation of CB was restrained and thus the filler–filler interaction was receded in vulcanizates prepared via the latex

way. Furthermore, although both W-CB and W-CBO vulcanizates were blended under the same condition, the difference in the surface properties of CB results in distinct dynamic properties. It can be observed from Figure 7 that the storage modulus of W-CB was higher than that of W-CBO when the deformation was relatively small; however, they finally almost reached to an approximate value when the strain increased to 20%. Based on Guth–Gold equation, Medalia[34] put forward that G' was a function of the storage modulus of pure gum (G_0) and the effective concentration of CB (φ_{eff}), while φ_{eff}, a sum of CB content and the occluded rubber, was determined by the filling amount of CB (φ) and DBP absorption value. Two formulas were shown as follows:

$$G' = G_0(1+2.5+14.1\varphi_{eff}^2) \qquad (2)$$

$$\phi_{eff} = \phi(1+0.02139DBP/1.46) \qquad (3)$$

After oxidation treatment, a decline in DBP absorption value of CBO was observed (111 cm^3/100 g, that of CB was 125 cm^3/100 g), which resulted in the decrease of effective concentration of CB, thus the storage modulus of W-CBO was smaller than W-CB at low strain according to the above equations. Nevertheless, when the strain reached to the point where the filler–filler interaction could be destroyed, the occluded rubber wrapped by the filler network would be released and therefore φ_{eff} returned to the normal level close to the filling amount of CB. As a result, the storage modulus of W-CB and W-CBO vulcanizates were nearly the same under a large deformation.
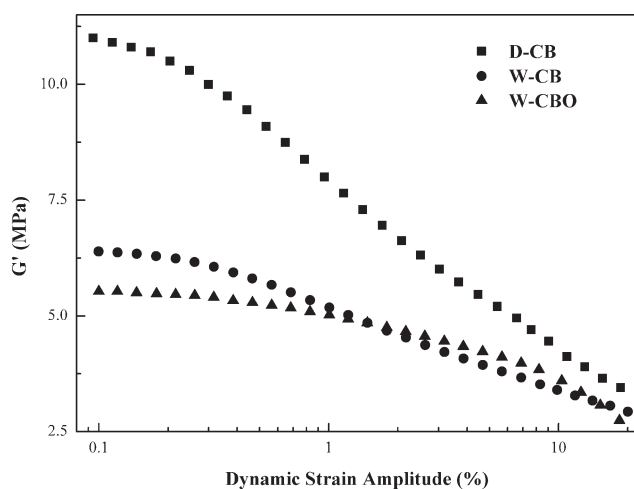
Figure 7. Strain dependence of G' at 11 Hz for D-CB, W-CB, and W-CBO vulcanizates (40 phr).
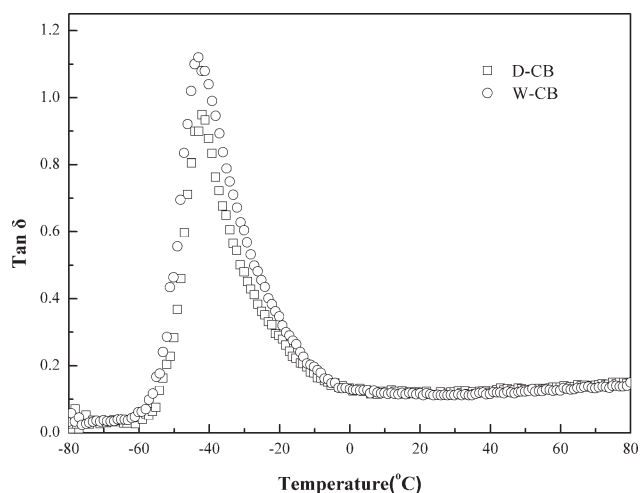
Figure 8. Dynamic mechanical spectrum of CB-filled NR compounds (40 phr).
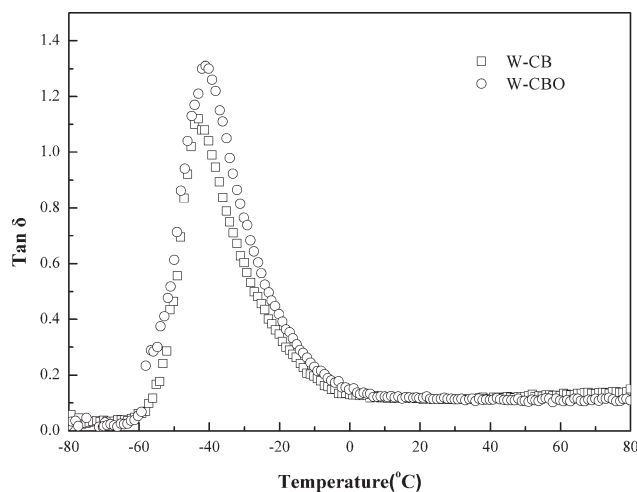
Figure 9. Dynamic mechanical spectrum at 11 Hz for W-CB and W-CBO (40 phr).

Dynamic Properties of Natural Rubber Reinforced by Hydrophilic CB

Figure 8 shows the temperature dependence of tanδ for CB-filled NR compounds. High hysteresis at low temperature (−60 to 0°C) which indicates an outstanding wet-skid resistance is a significant parameter to the CB-filled tire tread. As shown in Figure 8, W-CB displayed a splendid wet-skid resistance in comparison with D-CB based on its higher loss factor at low temperature. The CB particles were prone to gather together and formed strong filler–filler network when CB was filled into natural rubber by a dry mixing process at a large loading content. A portion of polymer molecules would be wrapped into this kind of network and lost its mobility, resulting in a reduction of molecule chains participating in the movement. As for W-CB vulcanizates, occluded rubber in the filler network would be quite less than that of D-CB based on the uniform dispersion of CB in the matrix according to the SEM result, which is responsible for the large loss factor in transition zone.

Figure 9 shows the dynamic mechanical spectrum at 11 Hz for W-CB and W-CBO. It can be observed that the transition peak of W-CBO moved to a high temperature in comparison with W-CB (from −43.1 to −41.1°C) and a high transition peak was found in W-CBO. These results were reasonable because that CBO would absorb more polymer chains based on the its peculiar surface properties including specific surface area and surface roughness. Thus higher temperature was needed for the chains to move and more frictions were created between fillers and polymer chains.

CONCLUSION

Natural rubber reinforced by poly(sodium-4-styrenesulfonate)-decorated CB with a latex compounding technique was prepared. CB could uniformly disperse in the matrix according to the result of scanning electron microscope. Physical and mechanical properties were improved in comparison with the vulcanizates fabricated by traditional dry compounding, ascribed to the homogeneous distribution of CB in matrix and an increase of bound rubber. A decrease in the CB storage modulus at low strain was discovered due to the decline of aggregation between fillers. Owing to the changes of the physical properties of CB surface, vulcanizate filled with oxidized carbon black via latex way exhibited higher mechanical properties and weaker filler network. Furthermore, higher hysteresis at low temperature was achieved according to the result of dynamic mechanical spectrum.

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