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Effect of Grafted Carbon Black on Properties of Vulcanized Natural Rubber

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Summary

To modify carbon black (CB) surface, *in situ* grafting of natural rubber (NR) onto the CB surface by solid-state method was used to get grafted carbon black (GCB). The vulcanization characters of NR compounds employed CB and GCB were investigated. Crosslinking density of vulcanized NR was measured by equilibrium swelling method. As a result, it was found that GCB could improve both cure rate and crosslinking density. Moreover, the mechanical properties of vulcanized NR filled with GCB were enhanced to a large extent compared with vulcanized NR filled with CB. No Payne Effect was observed in GCB filled NR compounds during dynamic properties testing, indicating that there was no filler network and GCB was dispersed uniformly in NR matrix, which was proved by SEM micrographs. Based on above results, it was considered that the grafting modification weakened filler-filler interaction and enhanced filler-polymer interaction.

Introduction

The mechanical properties of the composite materials, which are composed of inorganic powder and organic polymers, depend greatly on the dispersibility of the inorganic powder in the polymer matrix and the interfacial interaction between the powder surface and the polymer molecules [1-3]. In order to get high property materials, a modification technology for the fine powder surface is very important to improve the dispersibility and interaction.

CB is the most commonly used filler for elastomer [4]. Generally CB particles tend to aggregate together and traditional manufacturing processes do not always create the desired surface properties that lead to its difficult dispersion in polymer. Accordingly surface modification is necessary. Therefore, various methods have been used to modify the surface characteristics of CB, such as chemical, electrochemical, and plasma treatment, in which the surface grafting of polymer onto CB is one of the effective methods [5,6]. CB is known to be a strong radical scavenger due to the presence of polycondensed aromatic rings and quinonic and phenolic oxygen [7], so propagating polymeric radicals can be easily trapped by CB surfaces during polymerization. Similarly polymers can also be grafted onto CB if they can dissociate and form radicals.

Usually there are two ways to graft polymer onto CB [8,9]. The first is "grafting onto" which involves either the reaction of reactive macromolecules with surface groups or the surface trapping propagating polymer chains. The second is "grafting from" which involves surface initiation then subsequent polymer grow from the surface. Tsubokawa and co-workers [10-12] have reported some other methods to graft polymer by CB surface trapping polymer radicals which was formed by thermal decomposition of some polymers such as azo, peroxide polymer and so on.

Many authors have reported their research work in the field of CB grafting, but there is still no report that GCB was applied in elastomer materials, which was because CB was generally grafted in solvent by which the output and efficiency of GCB production was greatly low. It is strongly required to propose a new way to modify CB, which can be effectively applied industrially, that is to say, to make GCB by solid-state method.

In previous work, *in situ* solid state grafting of decomposed NR onto CB surface was investigated [13,14]. The objective of present work was to understand the effect of GCB on its dispersibility and properties of NR vulcanizates. So the vulanization characteristics of NR were investigated. The mechanical properties and dynamic mechanical properties were also studied.

Experimental

Materials and Sample Preparation

CB, intermediate super abrasion furnace black (ISAF, grade N220) was supplied by Cabot Chemical Industry LTD. (USA). NR (RSS 3) was purchased from Teck Bee Hang (Thailand), having Moony viscosity (M_L 1+4 at 100°C) of 80 and Mw of 1200000. All other raw materials used were commercial grade.

NR-grafted CB (GCB) was made in Haake Rheomix600p internal mixer using a chamber of 70cc by solid state grafting method [13]. In this study, the weight proportion of NR and CB is chosen to be 1:1. After NR was decomposed for 15 minutes at applied high temperature and certain screw speed, CB was added to blend with decomposed NR, and then the GCB was obtained.

GCB was filled into NR according to the formulation as Table 1 without any other treatment after it was prepared in Haake mixer. Compounding was performed in an open two-roll mixing mill (φ160) at a friction ratio of 1.2. Mixing time of GCB and NR was 10 minutes while mixing time of CB and NR was 25minutes.

Table 1 Formulation of NR compounds

Ingredient	Compound (phr) [a]
NR	100.0
Zinc oxide	5.0
Stearic acid	2.0
Antioxidant (AO-20)	2.0
Carbon black	Variable
Accelerator CZ[b]	0.4
Accelerator DM[c]	1.0
Sulfur	2.5

[a] phr, parts per hundred parts rubber.
[b] N-cyclohexyl-2-benzothiazole sulphenamide.
[c] dibenzothiazole disulfide.

Grafting Percentage Determination

In order to determine the grafting percentage of GCB, which can be calculated from thermogravimetric analysis (TGA) results [9], GCB must be isolated from ungrafted polymer as following procedure. GCB was extracted in a Soxhlet apparatus with toluene for more than 100 hours until no more NR could be detected in the extracted solvent. The percentage of grafting was determined according to equation (1).

$$\text{Grafting (\%)} = (A/B) \times 100\% \qquad (1)$$

Here A (g) was the amount of NR grafted onto the CB, which was determined by weight loss when B (g) GCB was heated at 500°C in TGA tests.

TGA tests were performed with a Netzsch TG 209 in a nitrogen atmosphere, being in the temperature range of between room temperature and 800°C and a rate of heating of 10 K min^{-1}. The mass of samples was between 6.0 and 10.0mg.

Vulcanization Characteristics [15]

The vulcanization characteristics of the NR compounds studied were determined by Monsanto100S anoscillating disk rheometer at 140°C.

Scorch time (ts_2) was taken as the time at which the rheometer torque raised 2 units from the minimum torque. Optimum cure time (t_{90}) was taken as the time at which the rheometer torque increased to 90% of the total torque change following curing of rubber.

Crosslinking Density [16]

Crosslinking density of NR compounds was determined by equilibrium swelling method. Vulcanized NR compounds weighing 0.25-0.3g were allowed to stand in excess benzene. After 5 days, swelling was stopped. The crosslinking density(γ) was determined according to the relation,

$$\gamma=[\ln(1-\psi_r) + \psi_r + \chi\psi_r]/Vs(\psi_r^{1/2} - \psi_r/2) \qquad (2)$$

Where χ was a parameter characteristic of interaction between the rubber network and the swelling. For NR –benzene system the value of χ could be taken as a constant (0.425). Vs was the molar volume of benzene that is 89.4cm^3/mol. ψ_r was the volume friction of rubber in the swollen NR vulcanizate, which could be calculated according following relation,

$$\psi_r = [(m_d-m_0\omega)/\rho_s]/[(m_d-m_0\omega)/\rho_r+(m_s-m_d)/\rho_s] \qquad (3)$$

Where m_d was the mass of the test specimen after drying for 5 days at laboratory temperature. m_0 was the original mass of the test specimen and m_s was the mass of the swollen specimen. ω was the mass friction of the filler and zinc oxide in the test specimen. ρ_r was the density of NR which was taken as 0.965g/m^3. ρ_s was density of solvent that was 0.865g/cm^3 for benzene.

Density of NR Vulcanizates

The density of vulcanized NR was measured on a Mettler Toledo AL/AB-N analytical balance. The vulcanized NR was cut into small samples about 1×1×0.2cm. The density measuring was carried out at 25°C. There were two steps in density determination. First the sample was weighed in air and its mass was recorded as A. Then this sample was immersed into water absolutely and its mass in water was recorded as B. The density of sample (ρ) was calculated according to following relation,

$$\rho = (\rho_0 - \rho_L)A/(A\text{-}B) + \rho_L \qquad (4)$$

Where ρ_0 was the density of water which is taken as 0.99707 g/cm^3, and ρ_L was the density of air taken as 0.0012 g/cm^3.

Bound Rubber

For determination of the bound rubber content, CB-NR masterbatches (without curatives) were kept at room temperature for 7 days for conditioning. After this period, the compound was cut into small pieces. About 0.2g of the sample was immersed in 25 ml toluene in a stainless-steel wire cage. The solvent was renewed on 4th day, and after 7 days, the samples were taken out of the solvent and dried to a constant weight in vacuum. The bound rubber percentage (BR%) was calculated by the following equation [17]:

$$BR\% = \frac{W_d - F}{R} \times 100 \qquad (5)$$

Where W_d was the weight of the dried gel, F was the weight of the filler in the gel (same as weight of the filler in the original sample), and R was the weight of the polymer in the original sample.

Mechanical Properties

Dumb-bell specimens were cut and tested according to ASTM D412. Tear strength was measured on unnotched 90-angle testing specimens according to ASTM D624. The tests were performed with an Instron 4465 universal testing machine at a crosshead speed of 500mm/min. Shore A hardness was measured with a Shore Instrument according to ASTM D2240-75.

Dynamic Mechanical Properties

Dynamic mechanical properties were measured by a UBM Rheogel E4000 dynamic mechanical analyzer. The strain dependence of the dynamic shear properties was measured at 30°C on sample specimen 6mm in width and length, 2mm in thickness. Each sample was scanned from low frequency to high frequency in turn. The applied frequency was 0.1,1,11 and 110Hz, respectively.

SEM

SEM images were taken by JEOL JSM 6360 scanning eletron microscope. Vulacanizate was broken in liquid nitrogen. Cross section surface was covered with a layer of Au-Pd by sputtering treatment before SEM observing.

Results and discussion

Vulcanization Characteristics

Figure 1 gives scorch time and optimum cure time of NR compounds at different loading of filler. Compared with CB filled NR, GCB filled NR system has shorter scorch time and longer cure time, which indicates that GCB could improve vulcanization properties of NR compounds. It is also get this conclusion by the cure rate index (CRI) values (Figure 2).

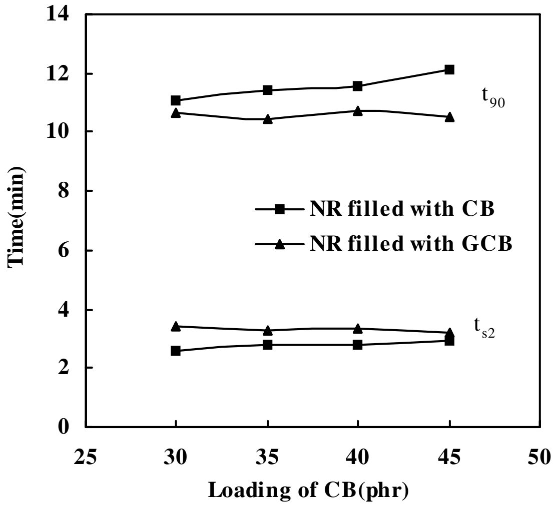

Figure 1 Scorch time and optimum cure time of NR filled with CB and GCB at different loading of filler (the grafting percentage of GCB is 15.9%.)

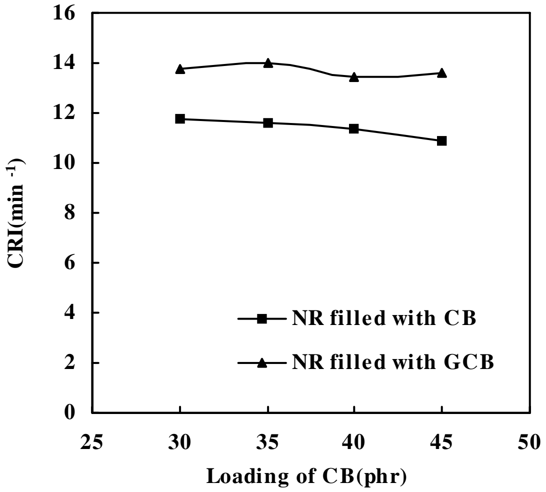

Figure 2 CRI values of NR filled with CB and GCB at different loading of filler (the grafting percentage of GCB is 15.9%.)

CRI, a kinetic parameters of vulcanization, is estimated according to the method reported by Menon[18].

$$\text{CRI} = 100/\ (t_{90}\text{-}t_{s2}) \qquad (6)$$

Figure 2 shows that the CRI values of GCB filled NR system are bigger than CB system, illuminating GCB could enhance cure rate of NR compounds. It is widely known that acidic materials in general retard the cure of elastomers [18]. There are many sorts of acidic groups such as hydroxyl group, ester group and quinine group on the CB surface, which absorb sulfuration accelerator so that the cure rate is retarded. After CB was grafted with decomposed NR, polymer chains enwraped the surface of CB, which prevented CB from absorbing accelerator. Then the cure rate of GCB copounds was improved.

Figure 3 shows delta torque curves of CB and GCB filled NR at different filler loading. Delta torque, the difference of maximum torque and minimum torque, is thought to be a measure of the crosslinking density, which increases steadily with increase of CB loading. It is found from figure 3 that delta torque values of GCB filled NR are higher than that of CB filled NR within the range of filler loading, suggesting that CB surface grafting would not only accelerate rubber vulcanization reaction, but also enhance its crosslinking density.

Table 2 gives crossinking density value of CB and GCB filled NR measured by equilibrium swelling method. The crosslinking density is found to increase with increasing filler loading. Similar to the result of figure 3, NR vulcanizates filled with GCB have higher crosslinking density values.

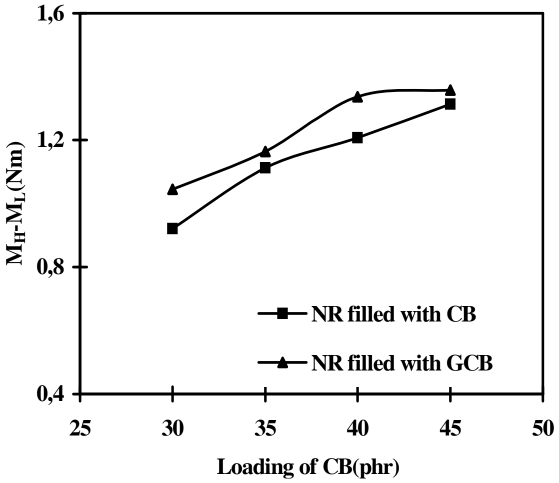

Figure 3 delta torque curves of NR filled with CB and GCB at different loading of filler (the grafting percentage of GCB is 15.9%.)

Table 2 Crosslinking density of NR filled with CB and GCB at different loading of filler (10^{-2}mol. cm^{-3})

Compounds	30phr	35 phr	40 phr	45 phr
NR filled with CB	2.505	2.653	2.694	2.747
NR filled with GCB[a]	2.704	2.828	2.803	2.856

[a] The grafting percentage of GCB is 15.9%.

Density of NR Vulcanizates

As it well known, there is much infinitesimal interspace between CB aggregates because the structure of aggregate is dendrtical, so the apparent density of CB is much lower than its intrinsic density. CB aggregates is thought not to be broken under general processing condition which lead to such result that much interspace also exist in CB filled rubber system. Figure 4 presents the density of different CB filled NR vulcanizates at different filler loading. The ideal density of NR compounds also given in figure 4, which is calculated when the density of CB is taken as its intrinsic density (1.86 g/cm^3). At applied filler loading scale, the density of GCB filled NR is higher than that of CB filled NR but lower than the ideal density. This result illuminates that CB aggregates were partly broken by powerful shear force during grafting in Haake mixer; therefore GCB was more compact than CB in NR vulcanizates.

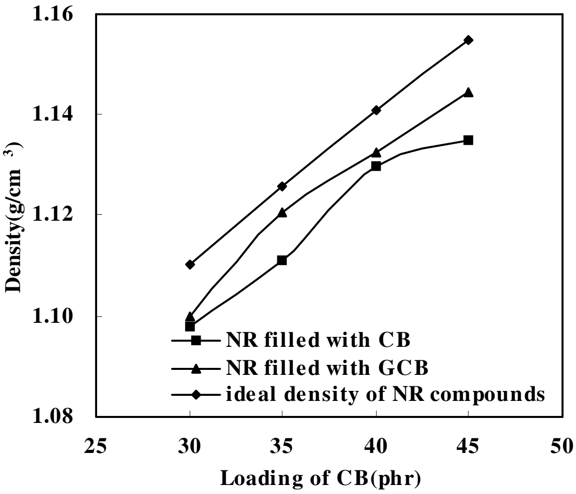

Figure 4 Density of NR filled with CB and GCB at different loading of filler (the grafting percentage of GCB is 15.9%.)

Mechanical Properties

The mechanical properties of vulcanized NR employed 35phr untreated CB and 35phr GCB are presented in Table 3. The results show that GCB improved both 100% and 300% modulus to a large extent. The modulus is a function of the filler loading, surface area, and structure of carbon black. At higher strain, the value also depends on the filler-polymer interaction. In this study with the same loading level of carbon black in both the formulations, the enhancement of the modulus in the GCB formulation should be attributed to the increase of filler-polymer interaction, which is induced by the grafting NR. The increase of filler-polymer interaction of GCB filled NR is approved by the increase of bound rubber content from 23.5% to 36%.

All tensile properties are improved except elongation at break. The elongation at break of GCB system is observed to decrease a little compared with the CB system, which can be attributed to the decomposition of NR chains grafted onto the CB surface. But this decrease is so mild that it does not influence the characteristic high elasticity of rubber materials. In addition, it is observed that GCB led to higher hardness and tear strength.

Table 3 Effect of GCB on Properties and Bound Rubber Content of NR compounds[a]

Compounds	Control[b]	GCB[c]
Tensile strength, MPa	27.8	30.5
Elongation at break, %	554	532
100% Modulus, MPa	1.5	2.3
300% Modulus, MPa	7.6	10.0
Hardness, Shore A	57	60
Tear strength, kN/m	75.2	93.6
Bound rubber content, %	23.5	36.0

[a] The grafting percentage of GCB is 15.9%.

[b] Control compound is filled with 35 phr commercial black.

[c] GCB compound is filled with 35 phr grafted carbon black.

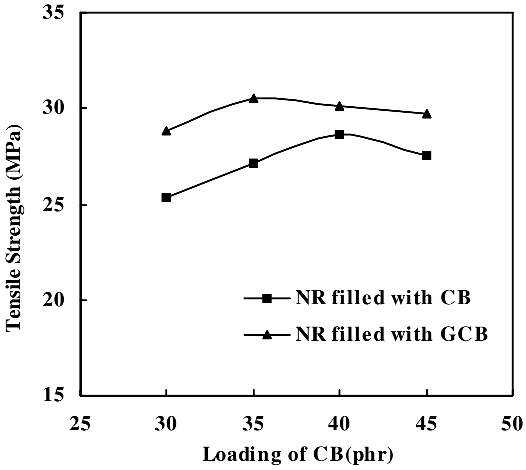

Figure 5 Tensile strength of NR filled with CB and GCB at different loading of filler (the grafting percentage of GCB is 15.9%.)

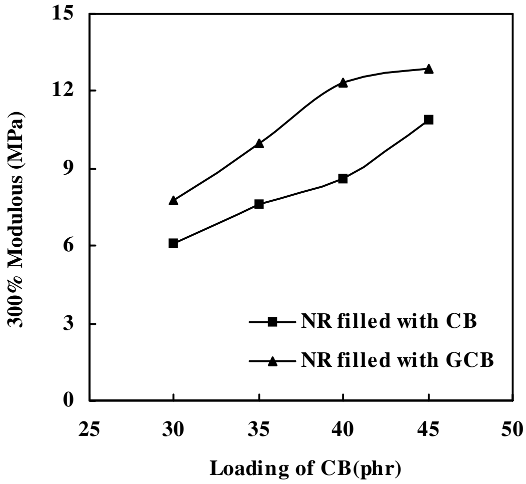

Figure 6 300% modulous of NR filled with CB and GCB at different loading of filler (the grafting percentage of GCB is 15.9%.)

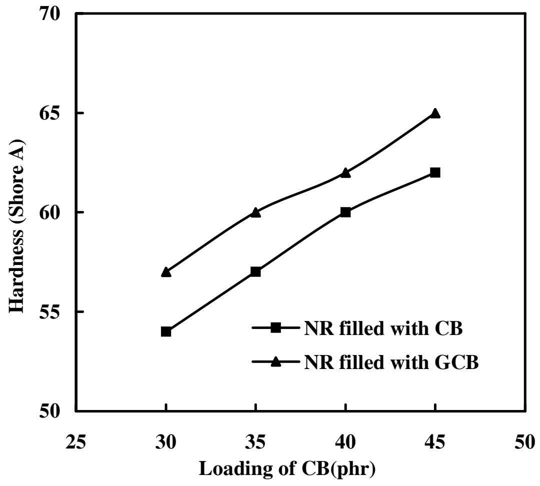

Figure 7 Hardness of NR filled with CB and GCB at different loading of filler (the grafting percentage of GCB is 15.9%.)

The mechanical properties of vulcanized NR employing different loading level of CB were also investigated. Figure 5 shows the effect of filler loading on the tensile strength of NR vulcanizates. The tensile strength of NR vulcanizates filled with GCB is higher than CB filled NR vulcanizates at all tested filler loading. And also the modulus at 300% of NR vulcanizates increases with filler loading increasing as shown in figure 6. The effect of filler loadings on the hardness of NR vulcanizates is shown in Figure 7. The hardness increases with increasing filler loading. GCB system shows higher value of hardness that is thought to be due to higher crosslinking density.

Effect of grafting percentage on mechanical properties of vulcanized NR

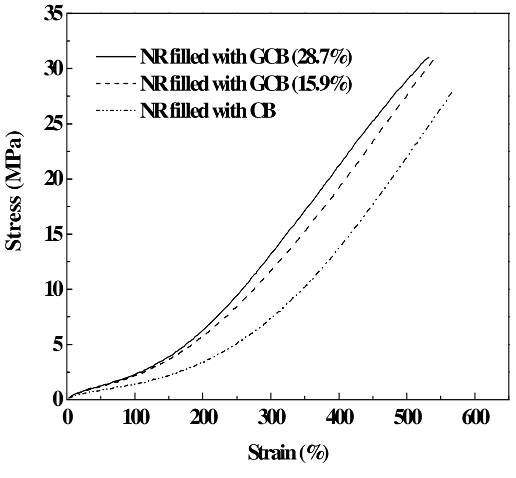

Figure 8 Stress-Strain Relationship of vulcanized NR filled with CB and GCB (The number in parenthesis is grafting percentage of GCB)

The relationship of strain-stress of vulcanized NR filled with CB and GCB is presented in Figure 8. The loading of filler is 35phr. There are two different grafting percentage of GCB was used. One is 15.9%, and the other is 28.7%. The results show that grafting onto CB lead to higher tensile strength. And moreover, GCB greatly improves 300% modulus of vulcanized NR compared with ungrafted CB that is due to the improvement of interaction between GCB and NR matrix. Unfortunately a little lower elongation at break is observed in GCB system. There is little difference in tensile strength and elongation at break when the grafting percentage increases. It can be seen that higher Grafting percentage lead to higher 300% modulus, which illuminates the increase of grafting percentage influences 300% modulus of vulcanized NR very much.

Dynamic Properties

CB particles conglomerates easily to form filler network in polymer matrix. Payne found that there was a noticeable decrease in the storage modulus of carbon black

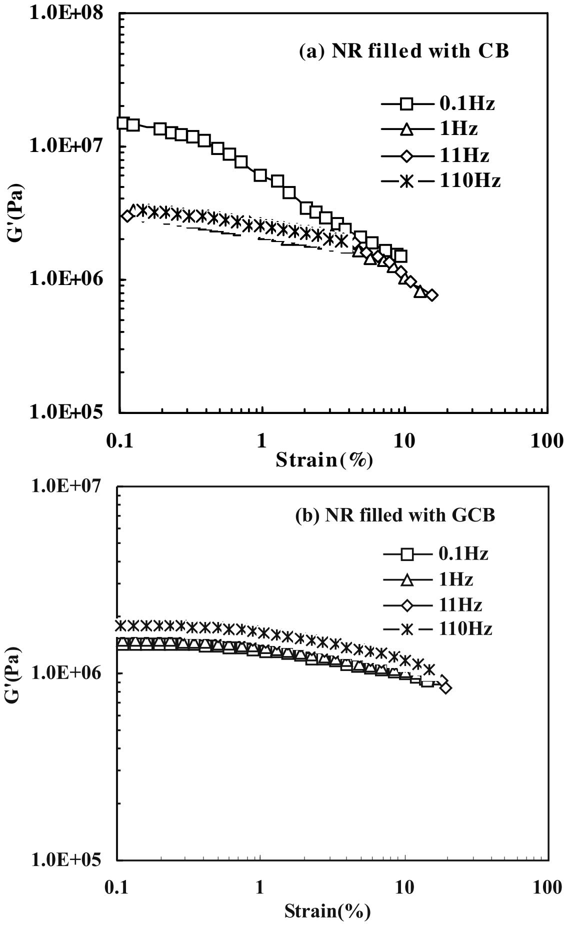

Figure 9 Relationship of the storage modulus (G') with strain (%) of NR filled with CB (a) and GCB (b) at different frequency (the grafting percentage of GCB is 15.9%.)

filled rubbery polymers with an increase in the amplitude of small strain oscillations in dynamic mechanical tests. This phenomenon was denominated “Payne Effect”[19]. Payne Effect is known to relate with filler network, so it is frequently used to research the filler dispersion state.

Figure 9 presents the Payne Effect of NR filled with CB (a) and GCB (b) at different frequency. Filler loading is 45phr. CB filled NR shows strong dependent with increased deformation. At all applied testing frequency, the storage modulus decreases quickly. As is known, polymer materials would behave more and more like hard materials if the frequency was enhanced continuously. But the modulus of CB filled NR decreased at high frequency after the first strain scanning at 0.1 Hz, suggesting there is a filler network in NR matrix and this network was rapidly destroyed with increasing strain. However, the storage modulus of GCB filled NR keep almost unchangeable and it shows a little rise when the testing frequency was increased, which reveals that GCB is dispersed uniformly so that no filler network is formed since the grafting layer weakens the interaction between CB particles and strengthens the interaction between CB and NR.

SEM

Figure 10 illustrates SEM micrographs of vulcanized NR filled CB (a) and GCB (b) at 35phr loading. It is obvious that the morphology of CB and GCB system are greatly different. As shown in figure 9 (a), ungrafted CB particles could not be dispersed well in NR matrix, moreover, CB particle domains have a very broad distribution and there are many large aggregates. The bad dispersion of CB is thought to be due to the weak interaction between inorganic CB and organic NR. On the other hand, GCB is dispersed uniformly into NR matrix and the domain size of dispersed phase is remarkably decreased, illuminating the interaction between GCB and NR increases because of organic polymer grafting.

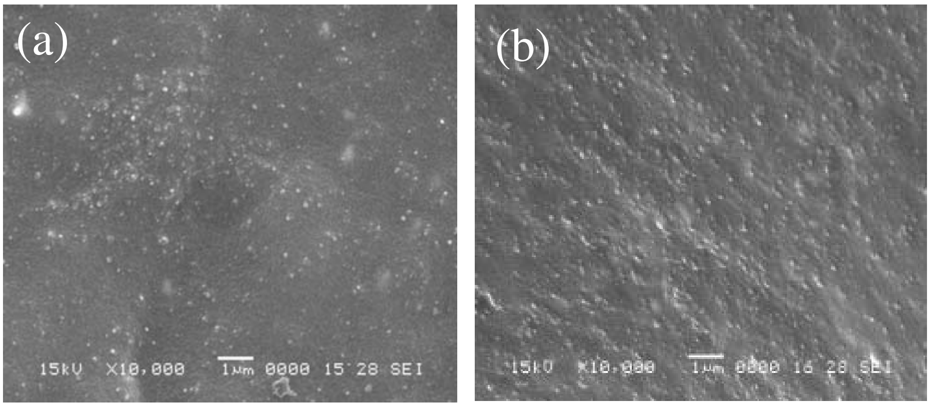

Figure 10 SEM micrographs of vulcanized NR filled with CB (a) and GCB (b) (the grafting percentage of GCB is 15.9%.)

Conclusions

The above results show that grafting of decomposed NR onto CB surface could effectively improve the cure rate and crosslinking density at the same time. No Payne

Effect is observed in GCB filled NR system due to better dispersion of filler. Compared with CB system, mechanical properties of NR vulcanizates filled with GCB are largly improved, which is because polymer grafting onto CB enhances the filler-rubber interaction and weakens filler-filler interaction.

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