

Influence of chloroacetate group on physical properties of natural rubber and its interaction with fillers

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ABSTRACT: Filler–rubber composites were prepared by mixing chloroacetylated natural rubber (CNR) with silica, carbon black (CB), or calcium carbonate using a two-roll mill. The interactions between the CNR and fillers, including silica, carbon black, and calcium carbonate, were characterized based on glass transition temperature (T_g) and shear storage modulus (G'). The results showed that both the T_g and G' values of the CNR–Si composite were found to be higher than those of the CNR–CB and CNR–CaCO₃ composites, indicating the existence of the CNR and silica interaction. The outstanding direct interaction between the CNR rubber matrix and silica without using a coupling agent was believed to be due to hydrogen bonds that formed between the hydroxyls of the silanol groups of silica and the carbonyls in the chloroacetate groups of CNR molecules. Moreover, it was also found that silica dispersed and distributed in the CNR matrix much better than in the natural rubber matrix. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43076.

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INTRODUCTION

Silica is widely known as a reinforced filler to improve the mechanical properties of elastomer composites, such as tear strength, abrasion resistance, and adhesion properties. However, the compatibility between silica and natural rubber (NR), which is a nonpolar elastomer, is low due to the noninteraction phenomena, whereas the interaction between a functionalized rubber such as nitrile–butadiene rubber (NBR) and silica in NBR–silica composites is found to be obvious due to the hydrogen bonds between the nitrile groups of NBR and the silanol groups of silica surfaces. The interaction based on the hydrogen bonding was found to correspondingly increase with the increase of the nitrile group content, resulting in the suppression of agglomerates in the composites.¹ Recently, many research works have been focused on the improvement of the compatibility between silica and NR by the creation of a chemical linkage using a coupling agent that usually was silane. However, the silica flocculation and the degree of silica–natural rubber interaction were found to depend on the type and the concentration of silane added. The addition of tetrasulfane influenced greater silica–natural rubber interaction and less flocculation of silica particles than did disulfane or a monofunctional silane.² Park and a coworker³ studied the crosslink density and thermal stability of styrene–butadiene rubber composites that were filled with treated silica with various

silane coupling agents. It was found that the composites treated with γ -methacryloxypropyltrimethoxysilane (MPS), i.e., the addition of an organic functional group, on silica surfaces showed greater crosslink density and thermal stability. Further research work clarified that the treatment of silica surfaces with bis(3-triethoxysilylpropyl)tetrasulphane (TESPT) improved the silica incorporation into the rubber matrix and the silica dispersion in the NR matrix⁴ and in the butadiene–styrene copolymer matrix.⁵

Thus far, new interfacial modifiers have been developed from NR via an epoxidation reaction. George *et al.*⁶ applied epoxidized NR (ENR) as a reinforcement modifier for silica-filled nitrile rubber (NBR). It was shown that NBR and ENR formed self-crosslinked structures. Moreover, ENR was found to link with silica particles under the vulcanization temperature, as confirmed by bound rubber, rheometric studies, and volume fraction. Incorporation of an optimum concentration of ENR in NBR–silica composites was claimed to give good mechanical properties comparable with those containing Si-69 [bis(3-triethoxypropyl)-silyltetrasulfide] as a coupling agent. Further work involving the addition of epoxidized poly(butadiene-*co*-styrene) (SBR) in the silica–SBR composite was studied by Rocha *et al.*⁷ The interaction between epoxidized SBR and silica was greatly improved due to the higher polarity characteristics of the epoxidized SBR. It has also been shown that the use of an epoxidized

SBR with just 7 mol % of epoxidation groups was enough to reduce the value of G' , the shear storage modulus, indicating a better interaction between the rubber matrix and silica. Cataldo⁸ had proposed the possibility to compound NR grade SMR20 with silica without the use of a silane coupling agent but with ENR. The improved mechanical properties were claimed to be in line with the polar nature of ENR that interacted strongly with the silica surface by a hydrogen bond. Sengloyluan *et al.*⁹ showed that the mol % epoxy and the content of ENR increased the interaction between silica and the NR grade “ribbed smoked sheet” and decreased silica–silica interaction. The addition of ENR-51 at 7.5 parts per hundred rubber content (phr) was found to show the best overall properties but significantly lower properties than the compound that was added with TESPT as a coupling agent. Furthermore, ENR was also used as an interfacial modifier for silica–NR (#3 smoked sheet) composites by Xu *et al.*¹⁰ It was claimed that the enhanced mechanical and dynamic mechanical properties could be attributed to the ring-opening reaction between the epoxy groups of ENR chains and Si–OH groups on the silica surface. On the other hand, the dispersion of silica in the NR matrix added with ENR was clarified to be improved, as evidenced from the scanning electron microscope (SEM) images of silica–NR composites with and without ENR for comparison. Another attempt was made to improve the poor dispersion of silica in NR by Choi and a coworker.¹¹ It was shown that adding chloroprene rubber to the silica–NR grade SMR CV60 composites increased the bound rubber content and the silica dispersion.

Numerous studies involving the chemical modification of NR were recent research works of interest. Modified NR could be expected to enhance the silica and NR interface interaction. Boochathum and a coworker chemically modified natural rubber latex (NRL) using O_3 , producing functionalized NR with ketone, aldehyde, or carboxyl groups at the molecular chain ends. These functional groups were found to enhance not only the processing¹² and mechanical properties¹³ but also the interface interaction between the silica surface and ozonolyzed NR by hydrogen bonding.¹⁴ Sahakaro and a coworker¹⁵ prepared the graft copolymer by melt mixing natural rubber (air-dried sheet rubber; ADS) with maleic anhydride (MNR). It was found that the use of MNR with appropriate maleic anhydride content dramatically reduced silica–silica interaction and hence improved silica dispersion, as confirmed by SEM micrographs. Luo *et al.*¹⁶ prepared the fumed silica–ENR composites by the mechanical mixing method. The interaction between fumed silica and ENR was investigated to be due to the hydrogen bond formed between the epoxy group of ENR and the silanol group of silica, resulting in better dispersion of fumed silica in ENR than in NR.

Various chemical modifications of NR had been performed to produce functionalized natural rubbers, such as hydrogenated, chlorinated, grafted, and epoxidized natural rubbers. This work reports the new modified NR, that is, chloroacetated NR or CNR, that was prepared by an epoxidation reaction followed by the addition of chloroacetic acid. Its molecular structure was confirmed by spectroscopy measurements using Fourier transform infrared spectroscopy (FTIR), 1H -NMR, and ^{13}C -NMR techniques. Studies on the interactions with various fillers that

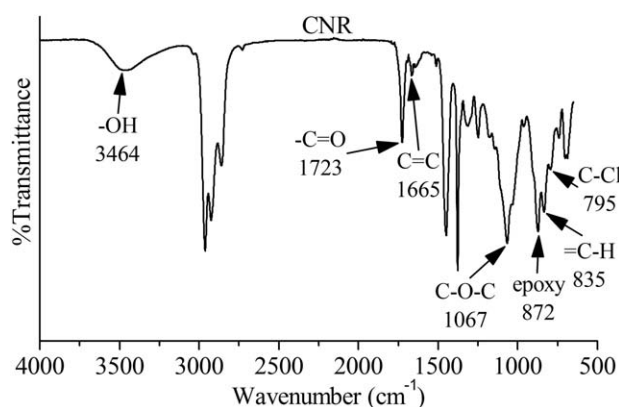


Figure 1. FTIR spectrum of CNR.

are commercially used in rubber-product industries, such as silica, carbon black, or calcium carbonate, were also performed.

EXPERIMENTAL

Materials and Reagents

The NR used in this study was high-ammonia natural rubber latex (NRL) with a dry rubber content of 60% that was purchased from Thai Eastern Rubber Co. Ltd. (Thailand). Dry NR was prepared from the coagulation of the NRL using formic acid. The precipitated silica (VN-3, 15 μ m), carbon black (N330), and calcium carbonate were purchased from United Silica (Siam) Co., Ltd. (Thailand), Thai Carbon Product (Thailand), and Ajax Chemical (Australia), respectively. The analytically graded formic acid, hydrogen peroxide, chloroacetic acid, and nonionic surfactant from Fisher Chemical (UK), Ajax Finechem (Australia), Sigma-Aldrich (USA), and Panreac (Spain), respectively, were used as received.

Preparation of Chloroacetated Natural Rubber

High-ammonia NRL (60% dry rubber content) was stabilized with a nonionic surfactant (14% w/v triton x-100) before adding the mixture of hydrogen peroxide and formic acid. The chemical ratio by mole based on dry rubber content of NRL, i.e., NR:HCOOH:H₂O₂, was 1:1:1. An epoxidation reaction was carried out at 40°C for 3 hours; subsequently, the epoxidized NRL obtained was added with chloroacetic acid (ClCH₂COOH) 25 mol % respectively to dry rubber content. Then the reaction was allowed to proceed for 1 hour at room temperature. The CNR prepared was agglomerated to a powder, and then the CNR powder was separated and washed with plenty of water until the pH of the washing water became 7. The CNR powder obtained was completely dried at room temperature.

Preparation of Filler–Rubber Composites

Filler–rubber composites were prepared by separately mixing the CNR with various fillers, including precipitated silica (Si), carbon black (CB), and calcium carbonate (CaCO₃) at a constant loading of 20 phr by using conventional two-roll mill mixing.

Structural Characterization of Rubber and Filler–rubber Composites

The molecular structure of CNR and its composites were characterized using FTIR (Nicolet 6700, Thermo Scientific) in the transmission mode and attenuated total reflectance mode (ATR). The

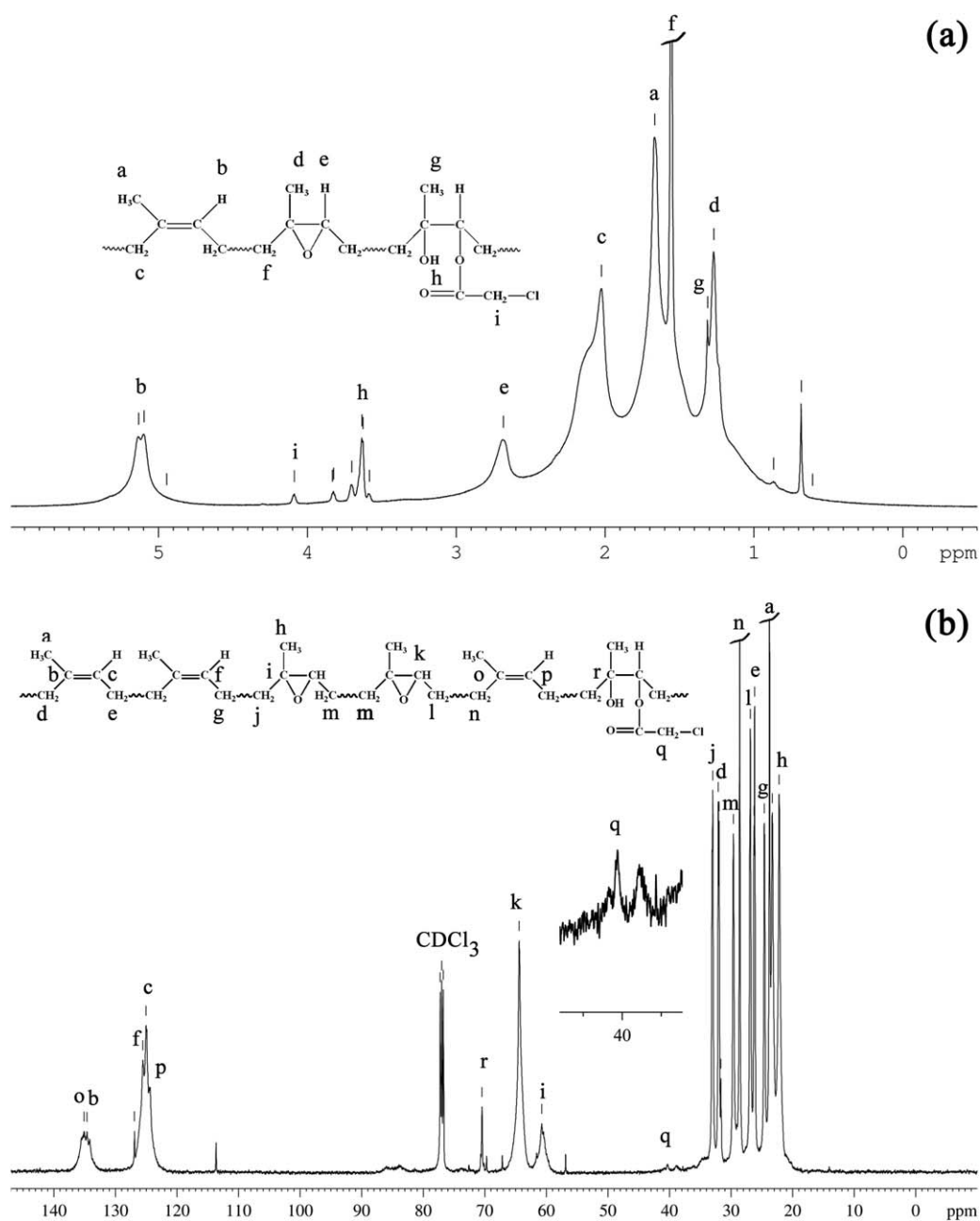


Figure 2. Spectra of CNR as measured by using (a) $^1\text{H-NMR}$ and (b) $^{13}\text{C-NMR}$ techniques.

spectra were recorded in the range of $4000\text{--}600\text{ cm}^{-1}$ with the resolution of 4 cm^{-1} .

The molecular structure of prepared CNR was also analyzed by using $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopies (AV-500, Bruker Biospin) at the temperature of $20 \pm 1^\circ\text{C}$. Samples were prepared by dissolving using CDCl_3 . The $^1\text{H-NMR}$ spectra were recorded at a frequency of 500 MHz. The spectral parameters used were as follows: 16 scans, relaxation delay of 2 s, spin rate of 25 Hz, and spectral size of 16 K with 32 K time domain size, and the $^{13}\text{C-NMR}$ spectra were recorded at a frequency of 125 MHz. The spectral parameters used were as follows: 4000 for number of scans (NS), relaxation delay of 1 s, spin rate of 25 Hz, and spectral size of 32 K with 32 K time domain size.

Thermal Stability Study

The thermal stability of CNR and nonmodified NR were measured by using thermogravimetric analysis (SDTA 851, Mettler Toledo). The rubber samples were measured under a nitrogen atmosphere and heated from 50°C to 900°C with a heating rate of $20^\circ\text{C}/\text{min}$.

Characterization of Filler–Rubber Interaction

The filler–rubber interaction was determined based on the immobility of rubber molecules via the glass transition temperature (T_g). The measurements were carried out under nitrogen flow by using differential scanning calorimetry (DSC1, Mettler Toledo). The temperature was calibrated using indium. About 5–10 mg of each sample was encapsulated in a hermetic pan

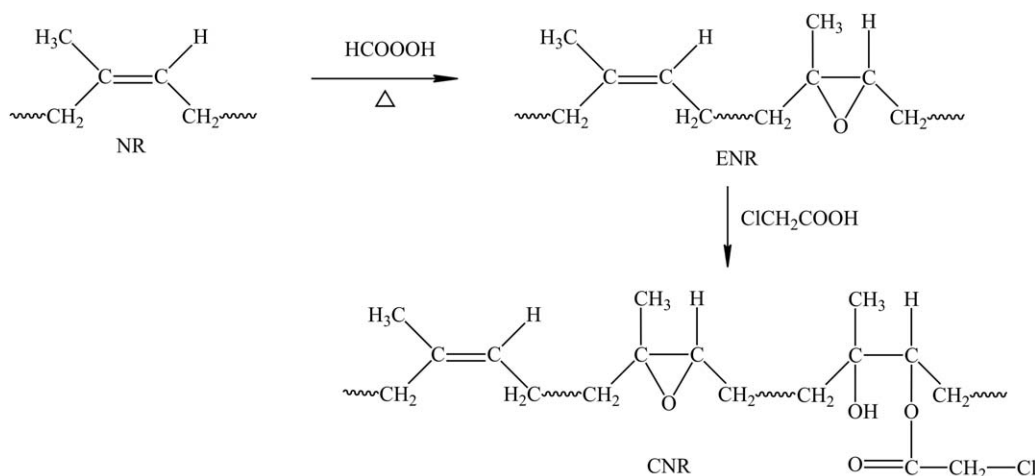


Figure 3. The proposed mechanism of the chemical modification of NRL producing chloroacetate NR.

and heated in the range from -100°C to 25°C at the scan rate of $10^{\circ}\text{C}/\text{min}$.

The filler–rubber interaction was also studied via G' in the strain sweep mode in the range of 0.28–1000% by using a rubber processing analyzer (RPA2000, Alpha Technologies). The measurements were carried out at a constant temperature of 50°C and at the frequency of 0.1 Hz.

Dispersion and Distribution Study of Silica in Rubber Matrix

The dispersion and distribution of the silica in the rubbers were investigated using a scanning electron microscope (JSM-6610LV, JEOL). Small pieces of the composites were immersed in liquid nitrogen, fractured into two pieces to create fresh surfaces, and then coated with gold. Photographs were taken at a number of different points.

RESULTS AND DISCUSSION

Characterization of Chloroacetylated Natural Rubber

To clarify the molecular structure of the CNR chemically modified from NRL, the rubber was characterized by using spectroscopy techniques, including FTIR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$.

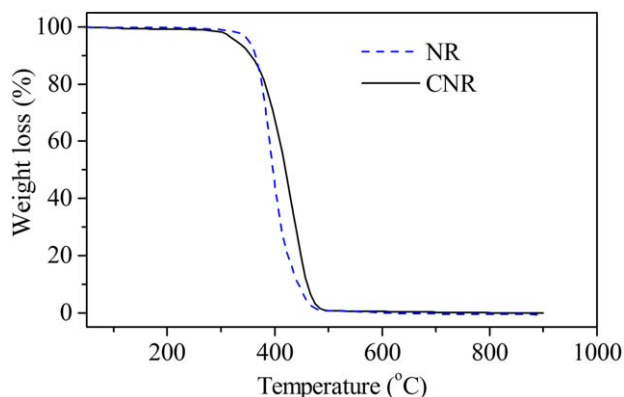


Figure 4. TGA thermograms of (---) NR and (—) CNR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 1 shows the FTIR spectrum of the CNR molecule. The important peaks included those at 3464 cm^{-1} for OH stretching, at 1665 cm^{-1} for $\text{C}=\text{C}$ stretching, and at 835 cm^{-1} for $=\text{C}-\text{H}$ out-of-plane bending. It also shows peaks at 795 cm^{-1} , 872 cm^{-1} , and 1067 cm^{-1} for $\text{C}-\text{Cl}$ stretching, the epoxy ring, and $\text{C}-\text{O}-\text{C}$ stretching, respectively. A strong peak at 1723 cm^{-1} for $-\text{C}=\text{O}$ of the chloroacetate pendant group was also clearly observed.

The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra confirmed the molecular structure of the CNR to be composed of isoprene, residual epoxy groups,^{17,18} and chloroacetate groups, which corresponds to the result analyzed from the FTIR measurement. The important peaks corresponding to the chloroacetate group showed at δ 1.31 ppm for CH_3-C , at δ 3.64 ppm for $\text{C}-\text{OH}$, and at δ 4.09 ppm for CH_2-Cl as analyzed by $^1\text{H-NMR}$ [Figure 2(a)] and at δ 40.30 ppm (q) for CH_2-Cl and at δ 70.46 ppm (r) for $\text{C}-\text{OH}$ as analyzed by $^{13}\text{C-NMR}$ [Figure 2 (b)]. The interpretation of the chloroacetate peaks was in agreement with previous reports,^{19,20} though the $\text{C}=\text{O}$ peak was not observed because of the drastically high number-average molecular weight of the CNR molecule, which is about $8.3 \times 10^5\text{ g/mol}$.²²

From the molecular structure characterized by the FTIR and NMR techniques, the molecular structure of the CNR chemically modified from the NRL was clarified to be composed of multifunctional groups including epoxy and hydroxyl present on the

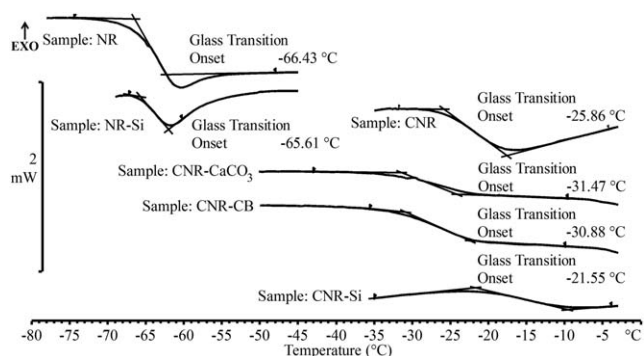


Figure 5. DSC thermograms of NR, CNR, and filler–rubber composites.

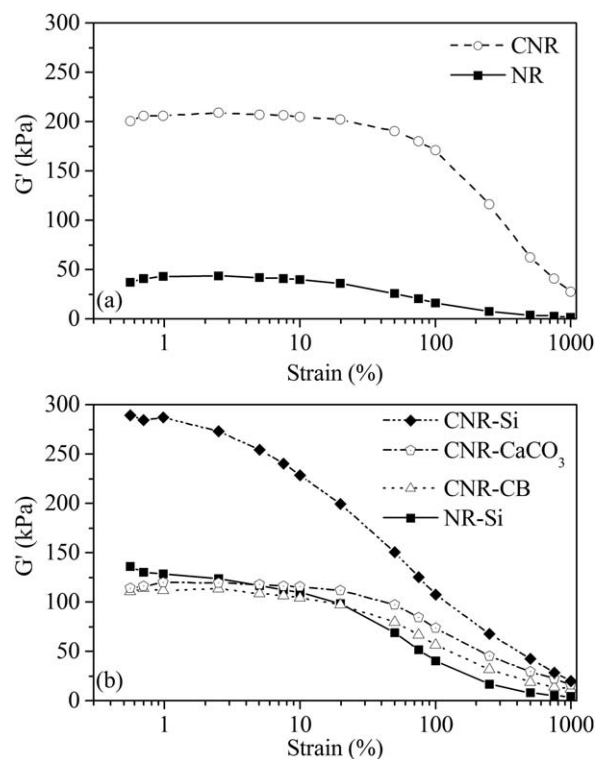


Figure 6. G' versus the strain sweep plots for (a) NR and CNR and (b) filler-rubber composites.

main chain and the chloroacetate present as pendant groups of a rubber molecule. The proposed mechanism of the chemical modification of NR producing the CNR is as shown in Figure 3.

The presence of the functional groups on an NR molecule was additionally supported by the evidence of T_g that is believed to be directly related to the immobilized molecules. The T_g of the CNR (-25.34°C) was found to be much higher than that of the NR (-66.55°C), which is due to the rigidity of the CNR molecules caused by the intramolecular interaction among the functional groups added to a rubber molecule. This interaction might be caused by a hydrogen bond formed between the carbonyl of acetate groups and the hydrogen of hydroxyl groups added on the rubber main chains.

Thermal Stability Study of CNR

The addition of chloroacetate groups on the NR was found to increase the decomposition temperature of NR. The onset decomposition temperature (T_d) of the CNR was determined to be 376°C , which was significantly higher than that of the NR ($T_d = 366^\circ\text{C}$). The increase of thermal stability of the CNR might be due to the reduction of double bonds present on the rubber molecules to form the chloroacetate functional groups. Two thermograms showing the thermal stability of the chemically modified NR, i.e., CNR, compared to that of the unmodified NR are shown in Figure 4. Although the NR initially decomposed a bit slower, it later decomposed faster than the CNR.

Filler-Rubber Interaction

In this study, the interaction between fillers and rubbers was investigated via T_g and G' values. It was obvious that CNR could

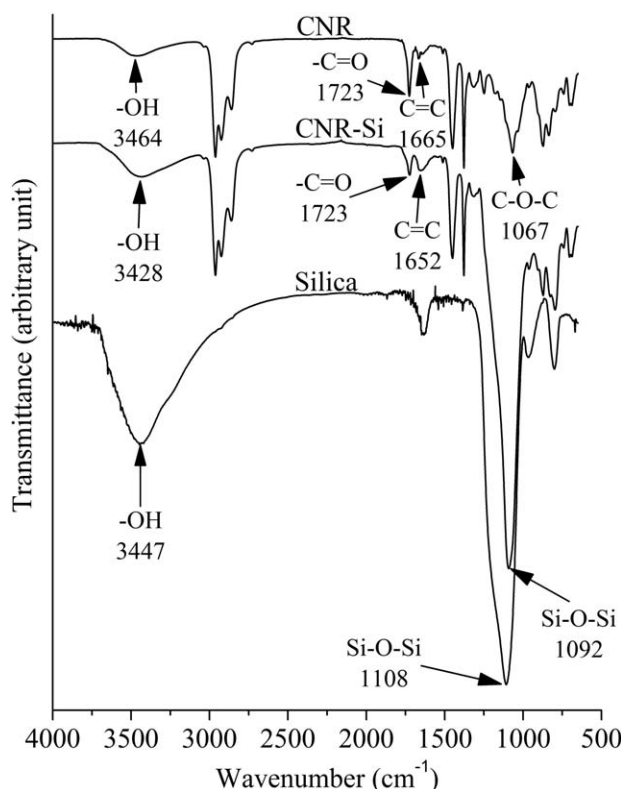


Figure 7. FTIR spectra of CNR, CNR-Si, and silica.

be compatible with silica without using a coupling agent. Regarding the results of T_g and G' , it is remarkable that the interaction between silica and the CNR resulting in the reinforcement phenomena was strongest. The drastic increase of T_g from -25.86°C for the CNR to -21.55°C for the CNR-Si is obvious (see Figure 5), due to the improved rigidity of the CNR molecules caused by the CNR-silica interaction, whereas there was no interaction evidence for the CNR-CB and CNR- CaCO_3 composites. The lower T_g values of the CNR in the CNR-CB and CNR- CaCO_3 composites that were found to be -30.88°C and -31.47°C , respectively, clarified that the CB and CaCO_3 distributed in the CNR matrix by locating in the space volumes of CNR molecules, causing more mobilized CNR molecules. On the other hand, the T_g of NR-Si (-65.61°C) was found to be slightly less than that of NR (-66.43°C). This is believed to be due to the incompatibility

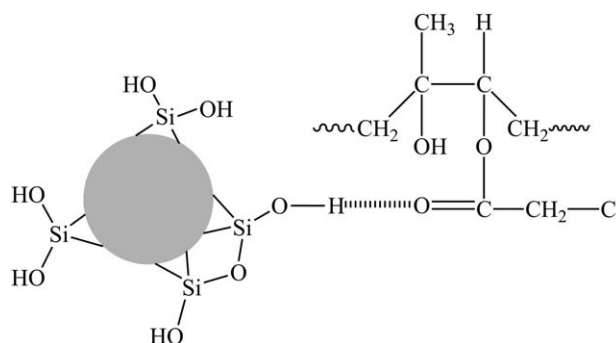


Figure 8. Proposed hydrogen bond between CNR molecule and silica surface in the composite.

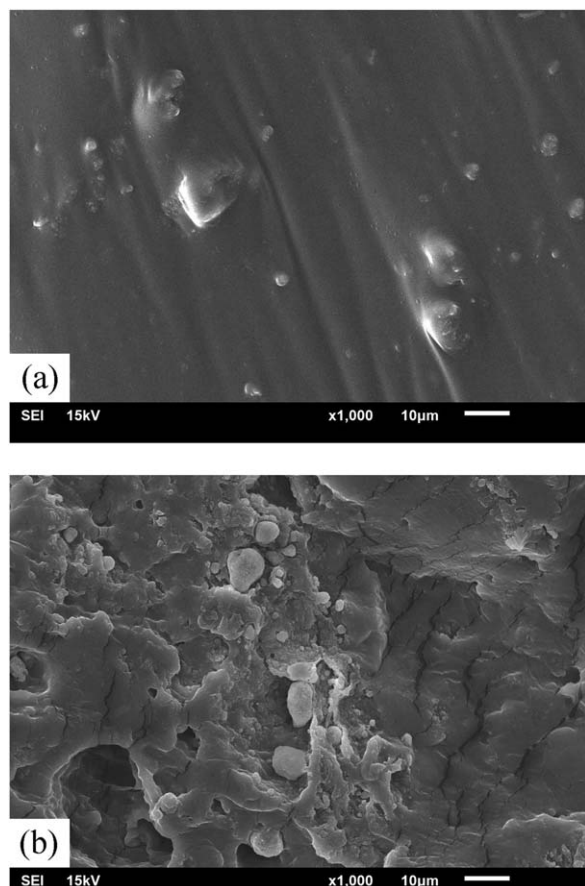


Figure 9. SEM micrographs taken on the surface fractures of (a) NR-Si composite and (b) CNR-Si composite.

between silica and NR as known. Therefore, the addition of chloroacetate groups on an NR molecule is proved to enhance the interaction with silica, resulting in higher reinforcement efficiency without using a conventional coupling agent. The DSC thermograms labeled with the T_g values of NR, CNR, and their composites are as shown in Figure 5.

Figure 6 shows G' at the % strain sweep for gum rubbers [Figure 6(a)] and filler-rubber composites [Figure 6(b)]. It is obvious that the NR-Si composite gave a considerably higher G' value than that of gum NR. This confirmed that the strong silica network was produced as expected. For the case of the CNR, it was found to be a different phenomenon that the increase of the G' value for the CNR-Si was tentatively due to the interaction between the CNR and silica, as supported by the significantly higher T_g of the CNR-Si described above. However, it was interesting that the G' values of CNR-CaCO₃ and CNR-CB were found to be lower than that of gum CNR because of the reduction of the CNR-CNR interaction. This evidence was in agreement with their lower T_g values obtained as mentioned above. As a result, it could be explained that the outstanding G' of CNR-Si was due to the hydrogen bond that was formed between the hydroxyl group present on the silica surface and the carbonyl group of acetate present on the CNR molecules.

The interaction between CNR molecules and silica particles was determined by FTIR spectra, as shown in Figure 7. The stretching of the frequency of the —OH group present on the silica

surface was found to shift from 3447 cm⁻¹ to 3428 cm⁻¹ in the composite of CNR-Si. The remarkable decrease of the hydroxyl peak is believed to be due to the characteristics of hydrogen bonds.²³ In addition, the reduction of the carbonyl (—C=O) peak of the chloroacetate group relative to the C=C peak of the CNR molecule in the CNR-Si composite also confirmed the hydrogen bonding. The proposed silica-CNR interaction due to the hydrogen bond between the —OH group in silica and the —C=O group in the CNR matrix is shown in Figure 8.

Dispersion and Distribution Study of Silica in the Rubber Matrix

The dispersion and distribution of silica were studied by SEM. The morphologies of the surface fraction of an NR-Si composite and a CNR-Si composite are shown in Figure 9(a) and Figure 9(b), respectively. It is remarkable that larger agglomerates and poor dispersion and distribution of silica in the NR matrix were clearly observed. This evidence is in agreement with the previous work by Ansarifar *et al.*,⁴ where silica showed better dispersion and distribution in the CNR matrix. This suggests that the chloroacetate groups added to NR molecules could enhance not only the reinforcement but also improve the dispersion and distribution of silica in the rubber matrix.

CONCLUSIONS

The addition of chloroacetate groups on a rubber molecule was found to improve the thermal stability of NR. The interaction between CNR and different fillers was determined via T_g and G' for comparison. The results showed that the CNR-Si composite gave much higher T_g and G' values, showing a better interaction than other composites, including CNR-CB, CNR-CaCO₃, and NR-Si. The considerably low T_g and G' values for the NR-Si composite were obvious due to the noncompatibility between silica and the nonpolar hydrocarbon rubber, i.e., NR. In contrast, the CNR-Si composite showed a strong interaction between silica and CNR molecules. This interaction was clarified to be due to the hydrogen bonds that were formed between the —OH groups present on the silica surface and the —C=O of the chloroacetate groups added on the natural rubber molecules. Furthermore, the dispersion and distribution of silica in the CNR matrix were observed to be much more improved than those in the unmodified NR matrix.

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