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Crosslinking via sulfur vulcanization of natural rubber and cellulose nanofibers incorporating unsaturated fatty acids

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ABSTRACT

The reinforcement of sulfur-vulcanized natural rubber using cellulose nanofibers (CNFs) was investigated. Natural rubber consists mainly of cis-1,4-polyisoprene, and becomes stretchable after vulcanization. Vulcanization was performed via crosslinking with the polyisoprene double bonds, using sulfur and unsaturated fatty acids (oleic acid) incorporated on the CNF surfaces, resulting in highly efficient reinforcement of the CNFs. The Young's modulus of rubber reinforced with 5 wt% oleoyl was 27.7 MPa, i.e., 15 times higher than that of neat rubber, while retaining a strain to failure of 300%. The coefficient of thermal expansion of 226.1 ppm/K for natural rubber was reduced to 18.6 ppm/K after the addition of 5 wt% of oleoyl CNFs.

Introduction

Stretchable materials are of interest for various applications; for example, stretchable sensors, scanners, and wearable computers are being developed as next-generation electronic devices.[1,2] Stretchable substances such as rubber are possible candidates for the substrate materials in such electronic devices. However, rubber has low rigidity and high linear thermal expansion compared with metals, silicon, and electrically conductive polymers. The functional materials that would be deposited on such rubber substrates could be destroyed or damaged by the temperatures used in the assembly and mounting processes because of the mismatch between the thermal expansions of the different materials.

The combination of high rigidity and low thermal expansion with the stretchable performance of rubber is also of interest for tires and other automotive components such as bumpers, which should keep their shape when subjected to large temperature differences while maintaining the excellent stretching properties required for shock and vibration absorption.

This can be achieved by reinforcement with cellulose nanofibers (CNFs). CNFs are a fundamental component of plant cell walls, and fibers of 4 to 20 nm width can be obtained by simple disintegration of paper pulp.[3] Because the nanofibers are made of semi-crystalline extended cellulose chains, they exhibit high elasticity (approximately 140 GPa), high strength (approximately 3 GPa), and low thermal expansion (approximately 0.1 ppm/K),[4] with a density of 1.6 g/cm^3.

Because of these excellent mechanical properties, and their high specific surface area, CNFs and cellulose nanocrystals (CNCs), which are whisker-shaped particles obtained by acid hydrolysis of cotton or wood pulp, have been studied for the reinforcement of thermosetting and thermoplastic resins.[4] The reinforcement of elastomers is of particular interest because high reinforcing efficiencies can be readily attained by the addition of small amounts of CNFs or CNCs.[5,6] Natural rubber reinforcement with CNCs has already been studied with and without vulcanization.[7–14] However, few studies using chemically modified CNFs have been reported, although CNFs have the advantage of higher aspect ratios than those of CNCs. The higher aspect ratios give continuous networks, and chemical modification would give good affinity with hydrophobic natural rubber.

Vulcanization is a process in which rubber is heated to induce a chemical reaction to form a three-dimensional network; this imparts the typical rubbery properties of resilience and strength. Sulfur is generally used to crosslink natural rubber because natural rubber consists of polyisoprene, which has many double bonds in its molecular chains and these react with sulfur to form a network.[15]

Pei *et al.* reported that crosslinking between the OH groups of CNFs and the hard segments of polyurethane elastomers effectively increases the Young's modulus and strength, without reducing the strain at break.[16] Rosilo *et al.* prepared CNCs that incorporated hydrocarbon chain brushes containing crosslinkable double bonds, and used them to make composite films in which the modified CNCs were dispersed within a polybutadiene rubber matrix via crosslinking by a UV-light-initiated thiol-ene click reaction. They found a percolative transition to modified-CNC-dominated behavior, and high rigidity was obtained at high CNC content.[17]

In this study, we attempted to achieve highly efficient reinforcement of natural rubber with CNFs that incorporated unsaturated fatty acids, which crosslinked with sulfur using the polyisoprene double bonds (Figure 1). The reinforcing efficiency of the CNFs was compared with those of hydrophobic CNFs incorporating saturated fatty acids and hydrophilic untreated CNFs.

Results and discussion

Fabrication of CNF-reinforced natural rubber

CNFs were prepared from refiner treated never-dried bleached softwood kraft pulp (NBKP) by grinding.[18] The crystalinity of CNFs was evaluated based on XRD patterns before and after grinding treatment and clarified that the crystalinity values, 70%, of NBKP did not changed significantly due to the grinding treatment. To study the reinforcing efficiency of natural rubber by CNFs, untreated CNFs, hydrophobic CNFs incorporating saturated fatty acids (stearic acid), and hydrophobic CNFs incorporating unsaturated fatty acids (oleic acid, which has the same carbon number as stearic acid) were prepared.[19] The weight gains resulting from the reactions were 76.8% and 67.3% for stearoyl and oleoyl, respectively. The variation of hydrophobicity of CNFs was studied before and after chemical modification using contact angle of water on the surface of compression molded CNFs disk. The contact angle at room temperature changed from 55 degree for untreated CNF to 93 degree for stearoyl CNF and 96 degree for oleoyl CNF.

Figure 2 shows the chemical structures of the chemically modified CNFs and the FT-IR spectra of untreated and chemically modified CNFs. The intensity of the peak at 1740 $\mathrm{cm^{-1}}$

(representing the C=O stretching vibration mode of the carbonyl group) increased significantly, clearly indicating that esterification had occurred. The degree of substitution (DS), calculated from the peak areas in the spectra, was 0.30 for stearoyl (st), and 0.27 for oleoyl (ole).

Preliminary X-ray diffraction analysis of the chemically modified CNFs indicated that esterification up to a DS of 0.4 does not change the crystallinity of the CNFs because the crystallinity after removal of the incorporated functional groups using NaOH was the same as that of untreated CNFs. This suggests that the chemical groups were mainly incorporated on the surface of the CNFs.

Field-emission scanning electron microscopy (FE-SEM) images of the chemically modified CNFs are shown with those of untreated CNFs in Figure 3. The saturated (stearic acid) and unsaturated (oleic acid) fatty acid were incorporated on the CNF surface, without significant agglomeration.

CNFs were added at concentrations of 1, 3, and 5 wt%, based on the weight of CNFs. The untreated hydrophilic CNFs were mixed with natural rubber latex in water, and then coagulated using formic acid. The chemically modified hydrophobic CNFs were mixed with a natural rubber solution in toluene. These mixtures were kneaded with stearic acid, zinc oxide, sulfur, and an accelerator, using a triple-roll mill, after removal of water or toluene. Sulfur vulcanization was achieved by hot pressing at 156 °C for 10 min.

The chemically modified, CNF-reinforced natural rubber was transparent at a CNF content of 5 wt%, as shown in Figure 4, indicating that the CNFs were well dispersed in the hydrophobic natural rubber.

Mechanical properties of CNF-reinforced natural rubber

The mean values and standard deviations of the tensile properties of the samples are summarized in Table 1. Figure 5 shows the tensile-mode nominal stress–strain curves for the natural rubber and CNF-reinforced natural rubbers. The numbers in parentheses are the Young’s moduli (MPa).

The reinforcing effect of the CNFs is clear, and the measured Young’s moduli changed significantly after CNF addition, as shown in Table 1. It is worth noting that not only the chemically modified CNFs, but also the untreated CNFs, reinforced the natural rubber, resulting in high strains at break, even after addition of 5 wt% CNFs. This indicates that the mixture of chemicals used in the triple-roll mill suppressed formation of agglomerates, which act as defects.

The reinforcing efficiency of the CNFs was improved by chemical modification. When 1 wt% of chemically modified CNFs was added to the natural rubber, the Young’s modulus increased three-fold, whereas a 1.3-fold increment was achieved by adding untreated CNFs. Further increases in the fiber content greatly increased the Young’s modulus, and the difference between the stress values at the same strain for the untreated CNFs and stearoyl CNFs became large. A comparison of the strain–stress curves of natural rubber + CNF3% and natural rubber + stCNF3% in Figure 5 provides a good example. The results suggest that good dispersion of CNFs as a result of the improved compatibility by the incorporated hydrophobic functional groups on the CNF surfaces increased the interphase area between the CNFs and natural rubber, and increased their interactions.

Furthermore, it is clear that the reinforcing efficiencies of oleoyl CNFs, which have double bonds, are higher than those of stearoyl CNFs, which do not contain double bonds. Figure 5 shows that at CNF contents of 3 wt%, the oleoyl CNFs showed a stress that was approximately 1.5 times larger than that of the stearoyl CNFs at the same strain. The Young's modulus of the rubber reinforced with 5 wt% oleoyl CNFs was 27.7 MPa, i.e., 15 times higher than that of neat rubber, while retaining a strain at break of 300%.

To compare the degrees of crosslinking in the composites, we measured the volumetric swelling of the neat rubber and the composites in toluene. The results showed that reinforcement with CNFs reduced the swelling from 374% to 272% for the stearoyl CNFs, and from 374.0% to 241.1% for the oleoyl CNFs. In addition, temperature-dependence measurements of the storage modulus, which were performed at 20–150 °C (Figure 6), i.e., at temperatures above the glass-transition temperature of vulcanized natural rubber, showed that the oleoyl CNF/rubber composite had a storage modulus that was 40–50% higher than that of the stearoyl CNF/rubber composite.

These results clearly indicate that the oleoyl CNFs had a higher level of interaction with the rubber than did the stearoyl CNFs; this provides evidence for the formation of crosslinks between the rubber and the CNFs, as a result of the double bonds of the oleoyl groups.

A noteworthy result was that, except in the case of addition of 5 wt% of oleoyl CNFs, the stress at break increased with increasing CNF content, without sacrificing the stretchable nature of the vulcanized natural rubber, as shown in Figure 5. It can be assumed that the CNFs were dispersed uniformly in the vulcanized natural rubber network, and deformed with the vulcanized natural rubber, while constraining deformation of the rubber network via the crosslinks generated between the CNFs and natural rubber. This increased the Young's moduli in the composites, while maintaining the stretchable nature of the vulcanized rubber. Another interpretation might be the interruption of the orientation of NR macromolecules during stretching and thereby constrained its crystallization. Further investigation is needed to clarify this interesting phenomenon.

Figure 7 shows the linear thermal expansion behaviors of the vulcanized natural rubber and the CNF 5 wt%/rubber composites. A significant reduction in the coefficient of thermal expansion (CTE) was achieved after the addition of only a small amount of CNFs. This reduction was more pronounced in the composites reinforced with oleoyl CNFs. As shown in Figure 7, the CTE of 226.1 ppm/K for the vulcanized natural rubber was reduced to 36.3 ppm/K after the addition of 5 wt% of stearoyl CNFs, and to 18.6 ppm/K after reinforcement with oleoyl CNFs; this illustrates the effects of crosslinking between the CNFs and the rubber. The CTE achieved using the oleoyl CNFs was double that of glass, and comparable to that of copper, which is typically used for electronic substrates.

This unusual combination of low CTE values and high stretchability opens possibilities for applications of these CNF-reinforced rubbers, not only for electronic devices, but also for automobile components such as bumpers and fenders, which are subjected to large temperature differences.

Materials and methods

Raw materials and fibrillation

The starting material was never-dried bleached softwood kraft pulp (NBKP) supplied by Oji Holdings Corporation (Tokyo, Japan). NBKP was fibrillated using a refiner until Canadian Standard Freeness was not more than 50 mL, as per TAPPI standard T227om-09. Native CNFs were prepared from the fibrillated NBKP via three passes of fibrillation of a 1 wt% aqueous suspension, performed using a grinder (MKZA6-2, Masuko Sangyo Co., Ltd., Japan) at 1500 rpm18).

Natural rubber latex (solid content 60 wt%) was obtained from the Sime Darby Plantation Co., Malaysia. N-methylpyrrolidone (NMP), toluene, formic acid, pyridine, stearic acid chloride, stearic acid, zinc oxide, and sulfur were obtained from Kanto Chemicals Co., Inc., Japan. Ethanol, dichloromethane, and N-cyclohexyl-2-benzothiazolesulfenamide were obtained from Wako Pure Chemical Industries Ltd., Japan. Acetone was obtained from the Sasaki Chemical Co., Ltd., Japan and oleic acid chloride was obtained from Sigma-Aldrich Japan K.K., Japan. All chemicals were used as received.

Chemical modification of CNFs

The esterification of CNFs were carried out based on Yoshida and Nakatsubo method.[19] An aqueous suspension of CNFs (2 kg, CNF content 1 wt%) was centrifuged at 7000 rpm for 20 min. The resulting precipitate (650 g, CNF content approximately 3 wt%) was poured into a large amount of acetone (600 g) and stirred. The suspension was centrifuged at 7000 rpm for 20 min. This acetone washing process was repeated three times to obtain a CNF suspension in acetone (CNF content 3–5 wt%).

This CNF suspension (CNF dry weight 3.0 g) was poured into an NMP/toluene solution (600 mL/300 mL), and the resulting mixture was distilled at 160 °C; nitrogen gas was passed through the reaction system to remove the toluene, acetone and residual water in the suspension. Pyridine (111 mmol) and acid chloride (55.5 mmol) were added to this CNF suspension in NMP. The reaction mixture was stirred at room temperature under a nitrogen atmosphere for 5 h, and then washed and filtered with a large amount of ethanol (or dichloromethane), to obtain the esterified CNFs.

DS values

IR spectra of dried thin CNF pellicles were recorded using a Spectrum One spectrometer (PerkinElmer Japan Co., Ltd., Japan) equipped with an attenuated total reflection attachment (Universal ATR, PerkinElmer Japan Co., Ltd., Japan). All the spectra were obtained by accumulation of 16 scans, with a resolution of 4 cm^{-1}, over the wavelength range 400–4000 cm^{-1}. The DS values of the esterified CNFs were calculated using the formula derived from the correlation of the DS obtained by the titration method and the area of the peak associated with carbonyl groups (1740 cm^{-1}).

Composite preparation

Untreated CNFs were mixed with natural rubber latex in water, and then coagulated using formic acid. Chemically modified CNFs were mixed with a natural rubber solution in toluene. CNFs were added at concentrations of 1, 3, and 5 wt%, based on the weight of CNFs. The mixtures were dried, and kneaded with stearic acid (1.5 phr), zinc oxide (2.5 phr), sulfur (3.0 phr), and accelerator (N-cyclohexyl-2-benzothiazolesulfenamide, 2.0 phr) for 20 min at 90 °C, using a triple-roll mill. Vulcanization was performed by hot pressing at 156 °C and 10 MPa for 10 min.

FE-SEM observations

Chemically treated and untreated fibrillated pulps were well dispersed in ethanol, and then filtered to make a thin wet pulp sheet; the sheet was then freeze-dried. The freeze-dried sheets were coated with an approximately 2 nm thick layer of platinum, using an ion sputter coater (JFC-1600; JEOL Ltd., Japan), and observed using FE-SEM (JSM-6700F; JEOL Ltd., Japan)

Tensile tests

The tensile properties of the samples were measured using an Instron 3365 universal materials-testing machine (Instron Corp., USA) on dumbbell-shaped specimens (JIS K6251-7, ISO-37-4, 1 mm thick) prepared from natural rubber or the composite sheets. The experiments were performed at room temperature (23 °C) and 50% relative humidity. The span and cross-head speeds were 20 mm/min and 200 mm/min, respectively. The initial Young's modulus values were calculated to be between ~0% and 20% in strain, where the strain increased linearly with stress. The results were the average of three measurements.

Dynamic mechanical properties

The temperature dependences of the Young's moduli of the composites were measured at 20–150 °C with a dynamic mechanical analyzer (DMS6100, SII Nanotechnology Inc., Japan), using the forced vibration method in tensile mode, under a nitrogen atmosphere, with a chuck distance of 20 mm, a frequency of 10 Hz, and a heating rate of 2 °C/min. The specimens were 40 mm long, 4 mm wide, and 1 mm thick.

CTEs

The CTEs were measured using a thermomechanical analyzer (TMA/SS6100, SII Nanotechnology Inc., Japan) with a chuck distance of 20 mm span. The measurements were carried out twice, under elongation in a nitrogen atmosphere, using a heating rate of 10 °C/min and a load of 3 g. The CTE values were determined at 20–140 °C during the second run. The specimens were 40 mm long, 4 mm wide, and 1 mm thick. The results were the average of three measurements.

Conclusion

The chemical modification of CNFs to provide hydrophobic properties resulted in highly efficient reinforcement of natural rubber. In particular, the incorporation of unsaturated fatty acid groups such as oleoyl on the CNF surfaces was effective after sulfur vulcanization because of the creation of crosslinks with the sulfur via the polyisoprene double bonds. The composites retained high strain-to-failure values, similar to that of vulcanized neat rubber. The combination of conflicting performances, high rigidity, low CTE values, and high stretchability opens up new potential applications of these CNF-reinforced rubbers in electronic devices, and for automobile components such as bumpers and fenders, which are subjected to large temperature differences.

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Figure Captions

Figure 1. Diagram of sulfur vulcanization reaction between polyisoprene and CNFs incorporating unsaturated fatty acids (oleic acid).

Figure 2. FT-IR spectra of untreated and treated CNFs: (a) CNFs, (b) stCNFs, and (c) oleCNFs.

Figure 3. FE-SEM images of (a) CNFs, (b) stCNFs, and (c) oleCNFs.

Figure 4. Natural rubber reinforced with chemically modified CNFs (1 mm thick, 5 wt% stearoyl CNFs).

Figure 5. Tensile-mode nominal stress–strain curves for natural rubber and CNF-reinforced natural rubber. The numbers in parentheses are the initial Young’s moduli (MPa).

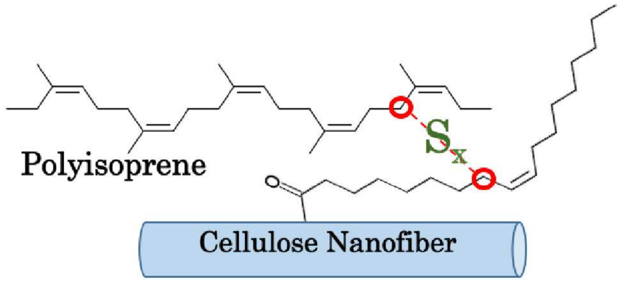
Figure 6. Temperature dependences of storage moduli of natural rubber and natural rubber reinforced with 5 wt% CNFs.

Figure 7. Thermal expansion behaviors of natural rubber and CNF-reinforced natural rubber. The numbers in parentheses are CTE values (ppm/K).

Table 1 Mechanical properties of natural rubber and CNF-reinforced natural rubbers.

	Yonug's modulus	Stress at break	Strain at break
	(MPa)	(MPa)	(%)
NR	1.7 (±0.0)	16.1 (±1.4)	623 (±14)
NR+CNF1%	2.2 (±0.1)	20.8 (±3.1)	658 (±41)
NR+stCNF1%	5.0 (±0.4)	15.2 (±2.1)	513 (±40)
NR+oleCNF1%	5.4 (±0.8)	18.8 (±1.7)	531 (±25)
NR+CNF3%	3.6 (±0.3)	28.4 (±2.8)	713 (±44)
NR+stCNF3%	9.6 (±0.8)	22.4 (±2.5)	537 (±37)
NR+oleCNF3%	12.7 (±1.9)	25.6(±1.0)	492 (±12)
NR+CNF5%	4.4 (±0.1)	30.3 (±0.4)	718 (±6)
NR+stCNF5%	18.3 (±1.0)	28.9 (±1.4)	530 (±30)
NR+oleCNF5%	27.7 (±4.4)	16.7 (±2.4)	251 (±69)

Mean value and standard deviation of three samples.



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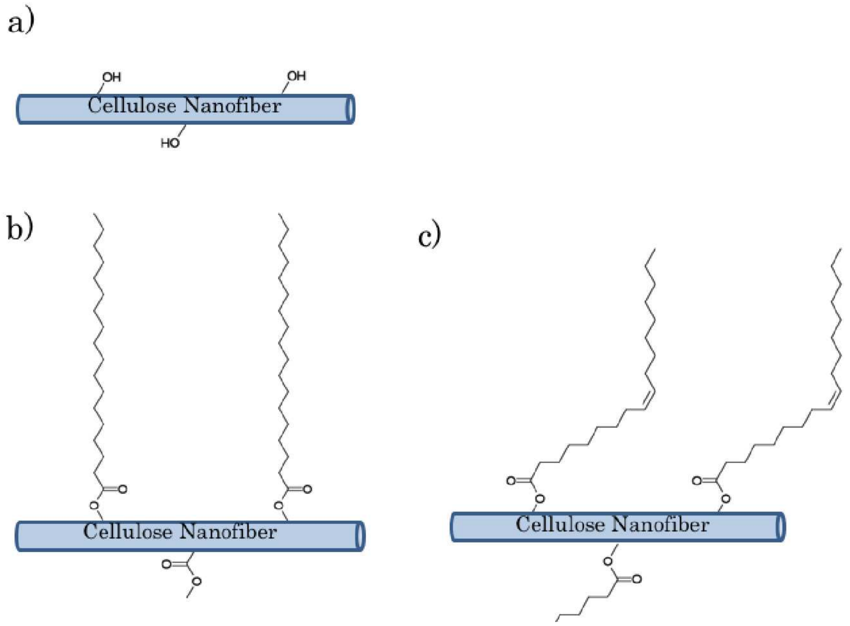

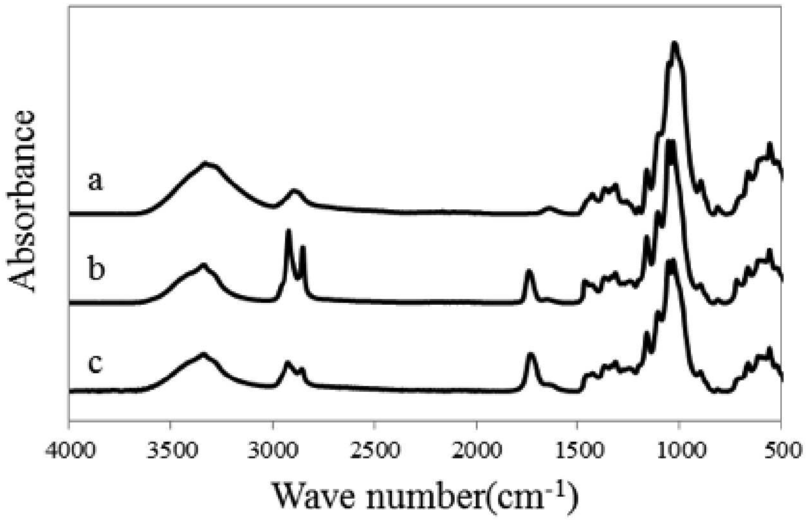

Figure 2. FT-IR spectra of untreated and treated CNFs: (a) CNFs, (b) stCNFs, and (c) oleCNFs.

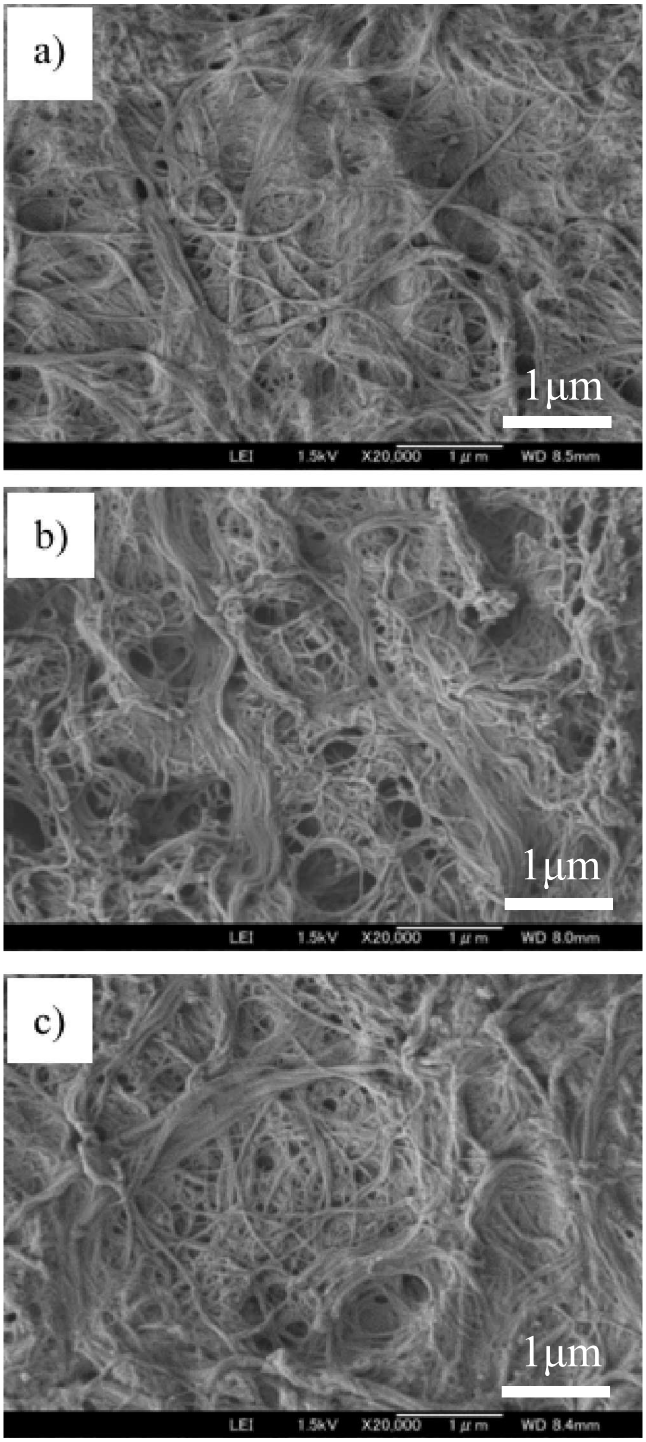

Figure 3. FE-SEM images of (a) CNFs, (b) stCNFs, and (c) oleCNFs.

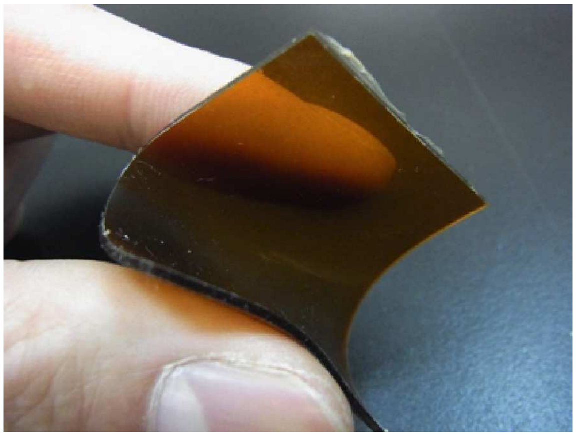

Figure 4. Natural rubber reinforced with chemically modified CNFs (1 mm thick, 5 wt% stearoyl CNFs).

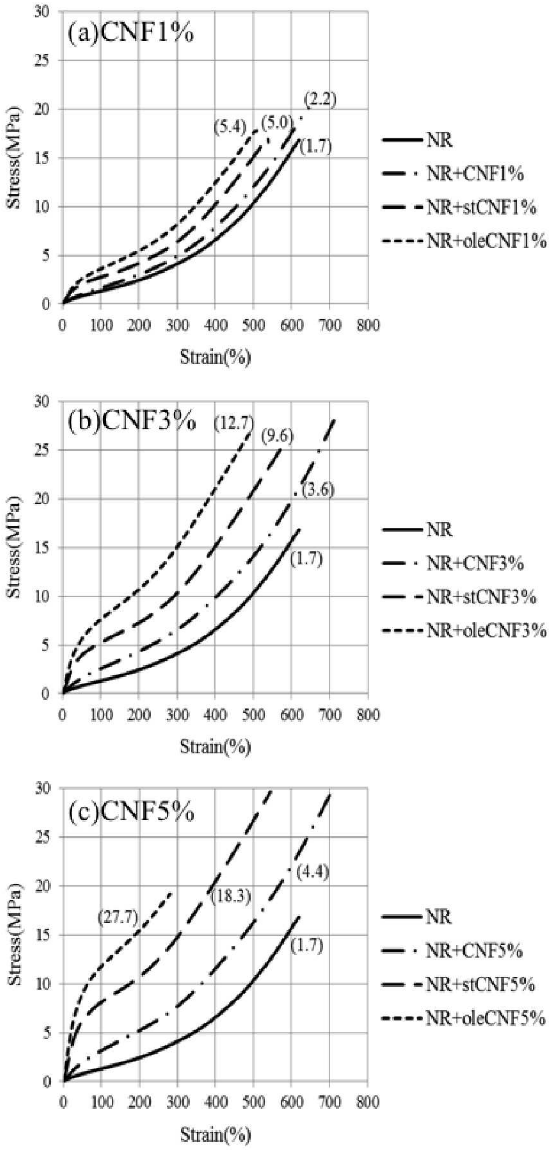

Figure 5. Tensile-mode nominal stress–strain curves for natural rubber and CNF-reinforced natural rubber. The numbers in parentheses are the initial Young's moduli (MPa).

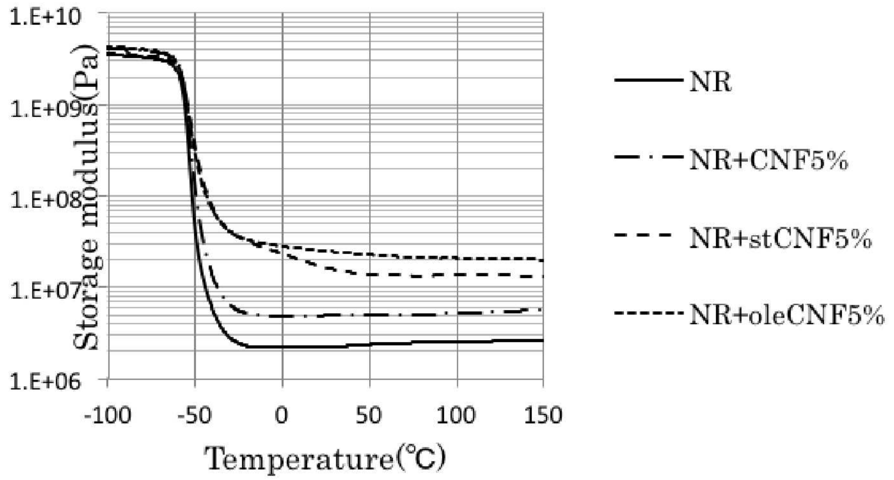

Figure 6. Temperature dependences of storage moduli of natural rubber and natural rubber reinforced with 5 wt% CNFs.

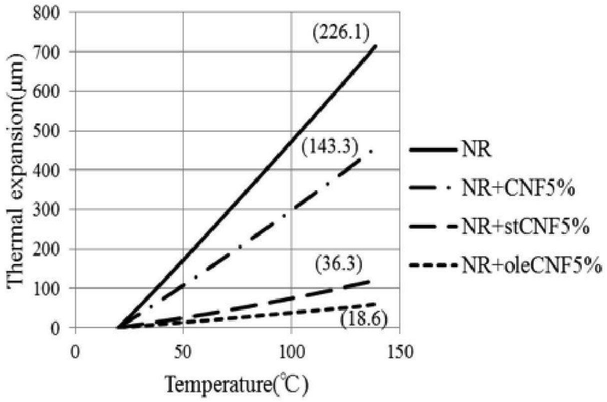

Figure 7. Thermal expansion behaviors of natural rubber and CNF-reinforced natural rubber. The numbers in parentheses are CTE values (ppm/K).