Preparation of Cardanol–Formaldehyde Resins from Cashew Nut Shell Liquid for the Reinforcement of Natural Rubber

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ABSTRACT: Natural rubber was reinforced with a high loading of a cardanol–formaldehyde resin prepared from cashew nut shell liquid. Cardanol–formaldehyde resins, both resoles and novolaks, were synthesized from cardanol, which was extracted from cashew nut shells. This was done by the condensation polymerization of cardanol and formaldehyde in the presence of base and acid catalysts. The cardanol–formaldehyde resole with the highest yield (ca. 75%) was prepared with a formaldehyde/cardanol molar ratio of 2.0 at pH 8.0 and 90°C for 8 h. The cardanol–formaldehyde novolak with the highest yield (ca. 80%) was prepared with a formaldehyde/cardanol molar ratio of 0.8 at pH 2.2 and 100°C for 7 h. Fourier transform infrared and ^{13}C-NMR were employed to characterize the chemical structures of the obtained cardanol–formaldehyde resins. The resins were compatible with natural rubber in various formulations. The cured behaviors of natural rubber blended with the cardanol–formaldehyde resole and novolak resins were investigated. The cured behaviors of cardanol–formaldehyde resole and cardanol–formaldehyde novolak samples were different, reflecting differences in their chemical reactivities. Furthermore, the incorporation of cardanol–formaldehyde resins into natural rubber provided significant improvements in mechanical properties such as the hardness, tensile strength, modulus at 100 and 300% elongation, and abrasion resistance. However, the elongation at break and compression set of the blends decreased as expected. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1997–2002, 2007

Key words: fillers; mechanical properties; reinforcement; resins; rubber fillers

INTRODUCTION

Cashew nut shell liquid (CNSL) is a renewable natural resource obtained from the cashew tree, *Anarcardium occidentale L.* In its natural form, crude CNSL is essentially a mixture of different phenolic compounds extracted from the shells of the cashew nut and is a good natural alternative to petrochemically derived phenol.[1,2] The major compounds of CNSL, which depend slightly on the geographical location of the tree, are anacardic acid, cardanol, and cardol (with the concentration of anacardic acid varying from 70 to 80%).[3,4] The structures of these components are shown in Scheme 1. Upon heating, anacardic acid is decarboxylated to produce anacardol, which, when hydrogenated, yields cardanol, as shown in Scheme 2.[5]

The aliphatic side chains of cardanol usually carry one, two, or three double bonds, and cardanol is a mixture of four components varying in the degree of side-chain unsaturation.[6,7] Because of this phenolic nature, cardanol can react with formaldehyde by condensation polymerization to produce cardanol–

formaldehyde (CF) resins.[8,9] CF resins are special phenolic materials having key properties such as high-temperature resistance, modulus retention at elevated temperatures, resistance to chemicals and detergents, high surface hardness, and low cost.[6]

CF reactions, like phenol–formaldehyde reactions, produce either thermosetting or thermoplastic resins, depending on the catalyst used and the molar ratio of the two reactants. A novolak resin, which is a two-step thermoplastic resin, can be obtained from the acid-catalyzed reaction when the reaction mixture contains less than 1 mol of formaldehyde/mol of cardanol. A resole resin can be obtained from the base-catalyzed reaction when the mixture contains less than 1 mol of formaldehyde/mol of cardanol.[8,10]

The use of reinforcing fillers, especially carbon black and silica, together with accelerated sulfur vulcanization, has remained the fundamental technique for improving the mechanical properties of rubber products. There has been some use of phenol–formaldehyde novolak resins as reinforcing fillers for natural rubber (NR) vulcanizates.[11] However, the most difficult problem in using phenol–formaldehyde novolaks is their incompatibility with less polar materials such as NR and some of its derivatives. The aliphatic side chains of cardanol reduce the polar effect of the phenolic resins and, therefore, increase the compatibility
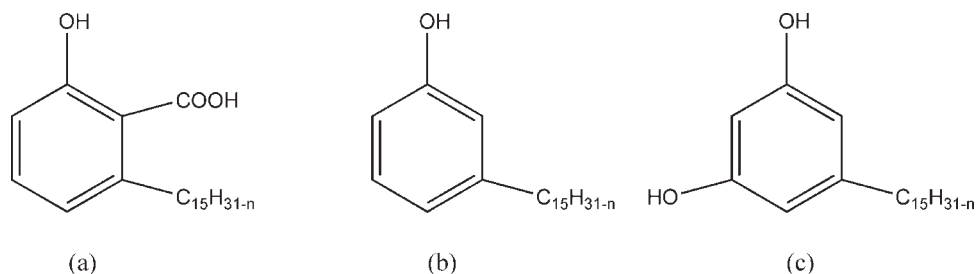
Scheme 1 Constituents of crude CNSL: (a) anacardic acids, (b) cardanols, and (c) cardols.

with NR.[6] Furthermore, the long side chains impart flexibility because of internal plasticizing, and this results in the formation of soft resins at elevated temperatures, unlike phenol–formaldehyde resins, which are hard.[8] In this study, the use of CF resins as reinforcing fillers in NR and their mechanical and thermal properties were investigated.

EXPERIMENTAL

Materials

Waste cashew nut shells obtained from the southern part of Thailand and analytical-reagent-grade hexane provided by Merck (Samutprakan, Thailand) were used in the CNSL preparation.

For the synthesis of the CF resins, aqueous formaldehyde (40%), an ammonium solution (25%), sulfuric acid (98%), toluene, and hexamethylene tetramine (HMTA) were analytical-reagent-grade and were obtained from Merck.

For rubber compounding, NR (STR XL) from Rayong Bangkok Rubbers (Rayong, Thailand), sulfur from Loxley (Bangkok, Thailand), zinc oxide from Univertures (Bangkok, Thailand), zinc stearate from Imperial Industrial Chemical (Bangkok, Thailand), and 2-mercaptobenzothiazole (MBT) from Flexsys (Akron, OH) were used. These chemicals were commercially available grades.

CNSL and cardanol preparation

By the immersion of the cashew nut shells in hexane for 1 week, CNSL was extracted as a dark, reddish-brown, viscous liquid. The liquid was then charac-

terized with a Nicolet Fourier transform infrared (FTIR) spectrometer.

The obtained CNSL (Madison, WI) was thermally treated at 130–140°C into decarboxylated anacardic acid, as shown in Scheme 2. The decarboxylated product was vacuum-distilled at 300–400 mmHg with a Buchi model R-205 rotavapor instrument (Flawil, Switzerland) to yield pure cardanol. The obtained product was characterized with FTIR spectroscopy and ^{13}C-NMR (200-MHz ACF, Bruker, Rheinstetten, Germany).

Resin preparation

CF resole and novolak resins were prepared from reactions between formaldehyde and cardanol; they depended on the formaldehyde-to-cardanol ratio and the reaction conditions employed.

CF resole resins were prepared, in the presence of ammonia as a catalyst, with molar ratios of formaldehyde to cardanol of 1.6, 1.8, 2.0, and 2.2. With each formaldehyde and cardanol molar ratio, the pH was adjusted to 7.6, 7.8, 8.0, 8.2, and 8.4, and the temperature of the reaction was also varied at 80, 90, 100, and 110°C. The reaction mixture was stirred continuously under a nitrogen atmosphere with heating for 8 h. Thereafter, the obtained resins were dried *in vacuo* at 70°C for 4 h. The resins were then ground into a fine powder. The yield of each reaction was investigated.

CF novolak resins were prepared, in the presence of sulfuric acid as a catalyst, with molar ratios of formaldehyde to cardanol of 0.6, 0.7, 0.8, and 0.9. At each molar ratio, the pH was varied at 1.8, 2.0, 2.2, and 2.4 with temperatures of 80, 90, 100, and 110°C. The reaction mixture was stirred continuously under
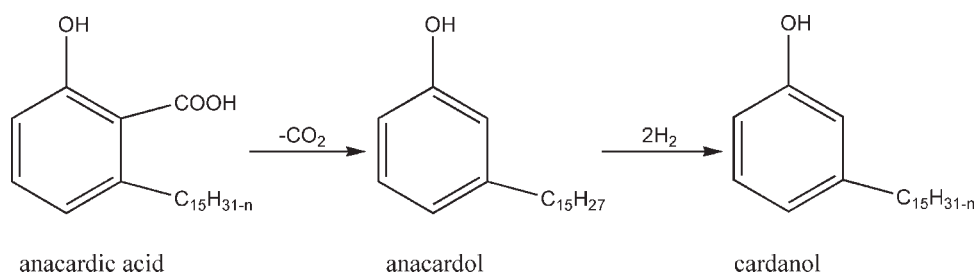
Scheme 2 Conversion of anacardic acid into anacardol and then cardanol.

a nitrogen atmosphere with heating for 7 h. Thereafter, the obtained resins were dried *in vacuo* at 70°C for 4 h. These were then ground into a fine powder. The yield of each reaction was investigated.

The thermal stability of each resin was examined with a Netzsch STA 409C thermogravimetric analyzer (Selb, Germany) under a nitrogen atmosphere from 0 to 600°C at the incremental rate of 20°C/min.

Rubber compounding and curing

Ground CF resins in various ratios were mixed with STR XL before curing. HMTA, a hardener, at the concentration of 10% (w/w) of the resin, was added to the CF novolak. The formulations are shown in Table I. The mixing processes were carried out with a two-roll mill at about 70°C. The scorch times and 95% cure times of the rubber compounds were determined with a Monsanto oscillating disk rheometer (MDR 2000, Akron, OH). Consequently, the rubber compounds were cured in a standard hot press.

Mechanical testing

The rubber compounds were compressed and cured into appropriate specimens. A JEOL JSM-5800LV scanning electron microscope (Tokyo, Japan) was used to investigate the morphology of the rubber products at 500×. The tensile properties, that is, the tensile strength, modulus of elasticity, and elongation at break, were investigated according to ISO 37:1994 (E) with an Instron testing machine (Model 1101, Canton, MA) equipped with a 500-N load cell at a testing speed of 500 mm/min. An extensometer was used to record the elongation of the dumbbell specimens. A Hampden APH-40 abrasion tester (Northants, UK) was used to determine the Akron abrasion resistance according to BS 903 Part A9 Method B. The weight loss after 1000 abrasion cycles was reported. The hardness was according to ASTM D 2240-97 with a Shore A Durometer (Shore Instruments Mfg., Freeport, NY). ASTM D 395 was followed for the compression set test. Each cylindrical test specimen was compressed to 25% of its original thickness and placed in an oven at 100°C for
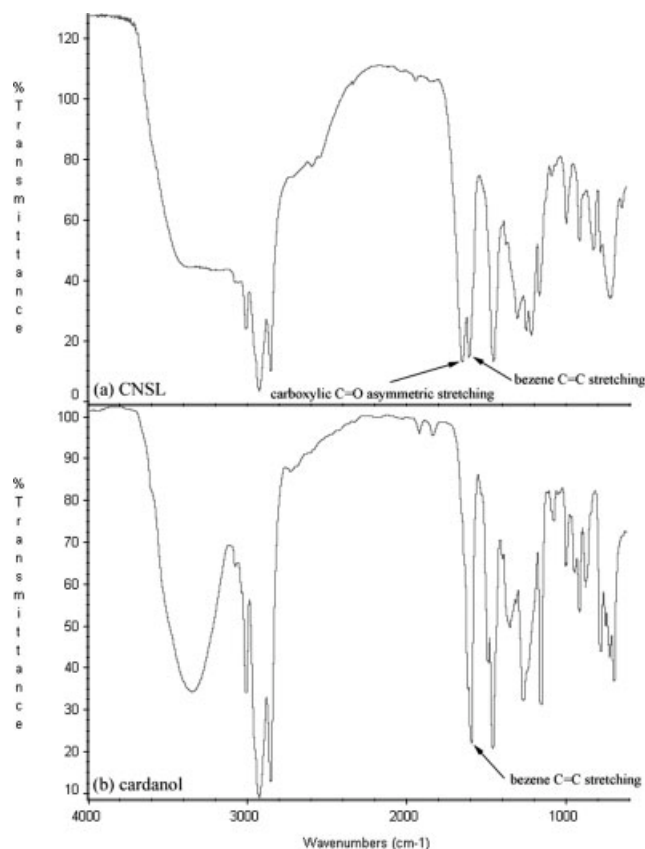

Figure 1 FTIR spectra of (a) CNSL and (b) cardanol.

22 h. The thickness of uncompressed specimens was used to calculate the compression set.

The tensile properties and hardness of the rubber products after 22 h of aging at 100°C in a Geers Ueshima A0103 rubber aging oven were also determined.

RESULTS AND DISCUSSION

CNSL and cardanol

The extracted cardanol, like CNSL, was able to dissolve in hexane, acetone, and toluene. It was characterized with FTIR and ^{13}C-NMR spectroscopy techniques. The FTIR spectra of CNSL and cardanol are shown in Figure 1. They are similar, except for the absence of the carboxylic C=O asymmetric stretching peak at 1670–1640 cm^{-1} in the FTIR spectrum of cardanol. This is due to decarboxylation of anacardic acids.

With the ^{13}C-NMR spectrum shown in Figure 2, we could confirm that the cardanol thus obtained was basically a monoene meta-substituted phenol having the empirical formula $C_{21}H_{29}O$.

CF resole and CF novolak resins

CF resole and CF novolak resins were synthesized under different conditions. Figure 3 shows FTIR spectra

TABLE I
Rubber Compound Formulation

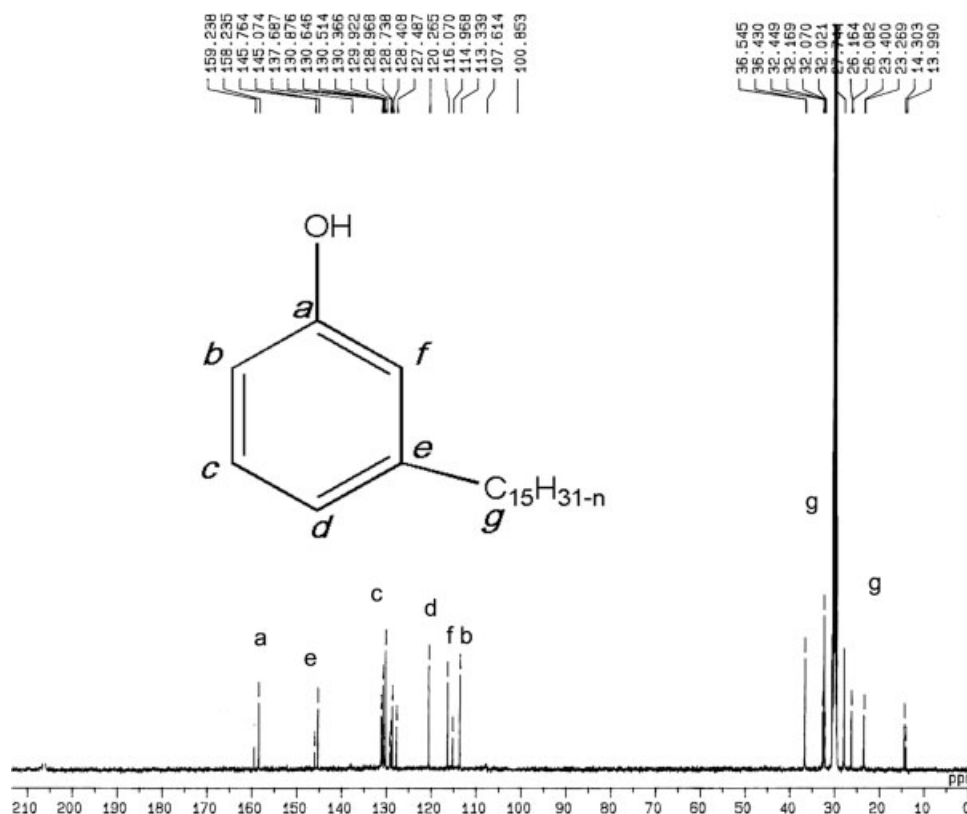|	Amount (phr)						
STR XL	100	100	100	100	100	100	100
CF resole	—	30	45	60	—	—	—
CF novolak	—	—	—	—	30	45	60
Sulfur	3	3	3	3	3	3	3
Zinc oxide	1	1	1	1	1	1	1
Zinc stearate	4	4	4	4	4	4	4
MBT	1	1	1	1	1	1	1

MBT, 2-mercaptobenzothiazole.

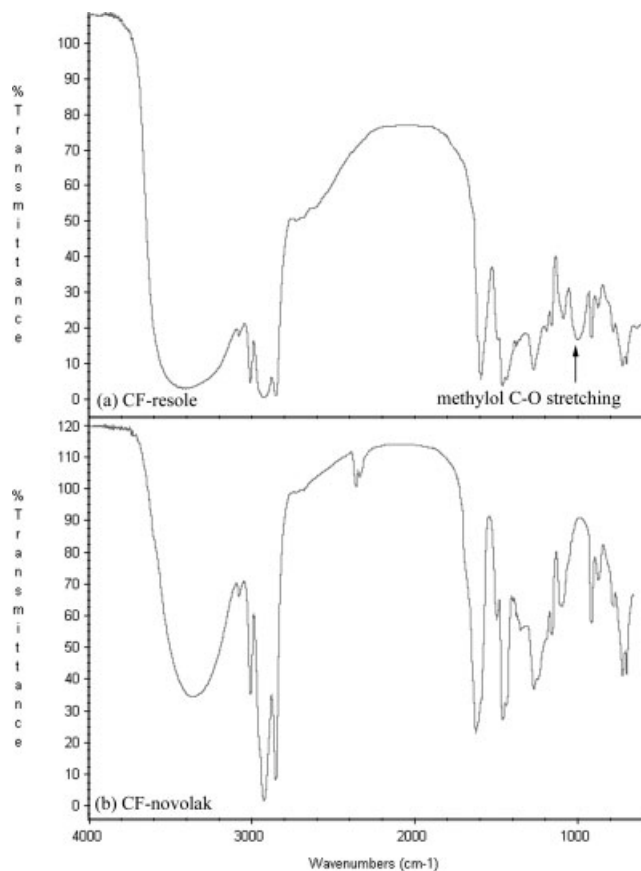**Figure 2** ^{13}C-NMR spectrum of cardanol in CDCl$_3$.

Figure 3 Spectra of (a) CF resole and (b) CF novolak resins.

of the obtained resins. The methylol C—O stretching peak at 1010–900 could be clearly seen only for resole resins because methylol groups are almost not presented in novolak resins. The yield at each condition was investigated, and the thermal degradation temperature of the resin was determined. For the CF resole resins, when the molar ratio of formaldehyde to cardanol was 2.0 and the reaction was carried out at pH 8.0 and 90°C for 8 h, the maximum yield and the highest degradation temperature of the product were 75% and 455°C, respectively. In the case of CF novolak resins, the maximum yield and the highest degradation temperature of the resin, 80% and 455°C, respectively, were obtained when the molar ratio of formaldehyde to cardanol was 0.8 and the reaction was carried out at pH 2.2 and 100°C for 7 h. On the basis of the results, we chose to use the resins synthesized under these conditions throughout the following experiments.

Curing characteristics

The scorch time and 95% cure time of the prepared rubber compounds are shown in Table II. The scorch time and cure time were reduced when the amount of the resins increased. The presence of resin particles promoted internal heat, which thus induced the reaction between the chemicals in the compounds. Menon et al.[1] explained that a progressive reduction in the

TABLE II
Cure Characteristics of the Rubber Compounds

	NR	CF novolak/NR			CF resole/NR		
		30	45	60	30	45	60
Scorch time (min)	7.08	3.83	2.88	2.21	6.33	6.33	5.79
Cure time (min)	16.58	7.96	7.17	6.17	12.17	11.58	11.58

scorch time of rubber compounds is due to the increased availability of unsaturated sites of the side-chain fragments of CF resins for cure reactions with those of the isoprene chains of NR. Different curing behaviors were found in the rubber filled with CF resole and CF novolak. In the case of CF-novolak-filled rubbers, HMTA was necessarily used as a hardener. The reaction between CF novolak and HMTA produced an essential amount of heat, which supplemented the vulcanization reaction. The vulcanization in the case of CF-novolak-filled compounds thus occurred faster than that in the case of CF-resole-filled compounds in which HMTA was not involved.

Mechanical properties

Table III shows the mechanical properties of cured rubber specimens before and after aging. The tensile strength of the filled specimens was higher than that of the unfilled specimen. It has been reported that the magnitude of the reinforcement is determined by the filler's ability to dissipate energy, which depends on the filler modulus as well as its adhesion to the matrix.[12] Possessing crosslinking characteristics of a thermoset material, including increasing tensile strength, decreasing elongation, and a fairly high modulus,[11] the CF resins thus improved the tensile strength of NR significantly. It has also been mentioned that this is probably due to the participation of unsaturated side-chain segments of CF resins in crosslinking reactions with those of NR.[1] The improvement of the abrasion resistance of the filled specimens was also due to the crosslinking between the unsaturated side-chain segments of CF resins and those of NR together with the entanglement between rubber and the long side chains of CF resins.

Scanning electron microscopy (SEM) micrographs, shown in Figure 4, revealed that the CF resins were uniformly dispersed in the matrix. It is believed that a uniform dispersion of fillers improves the degree of reinforcement.[13] However, the tensile strength decreased when the amount of the CF resins was increased because the rubber compounds were too dry and thus it was too difficult to form a continuous phase. CF-novolak-filled rubbers possessed higher tensile strength than CF-resole-filled rubbers as CF novolak contained stiffer crosslinks. The elongation at break of filled specimens was lower than that of unfilled ones. As the loading of CF resins rose, the elongation at break increased because of the plasticizing effect of the unsaturated side chains of the CF resins, which may have enhanced the segmental mobility of NR.[1] The stiffer crosslinks between CF novolak and HMTA caused the elongation at break of the CF resole to be less than that of the CF novolak. The modulus at 100 and 300% elongation behaved in the same manner as the tensile strength.

The CF-resin-filled rubbers showed higher hardness than the unfilled ones. Increasing the filler loading increased the hardness values. The CF-novolak-resin-filled rubbers possessed higher hardness than the CF-resole-resin-filled rubbers as novolak contained stiffer crosslinks. The compression set of the CF-resin-filled rubber was higher than that of unfilled NR. The interaction between the rubber and filler reduced the resiliency of the NR molecular chains. When the amount of CF resins increased, the compression set was lower. The increasing resiliency was due to the plasticizing characteristics of the long chains of the CF resins.

TABLE III
Mechanical Properties of Rubbers Before and After Aging

|		NR	CF novolak/NR			CF resole/NR		
			30	45	60	30	45	60
Tensile strength (MPa)	Before aging	19.6	29.5	25.8	25.1	27.3	27.8	19.0
	After aging	16.9	27.8	23.9	23.9	24.0	22.2	18.2
Elongation at break (%)	Before aging	971.5	725.2	792.4	873.0	782.4	871.0	931.0
	After aging	594.7	643.0	719.0	775.0	664.2	757.0	805.0
Modulus at 100% elongation (MPa)	Before aging	1.08	1.27	1.46	1.75	1.12	1.51	1.62
	After aging	0.88	1.49	1.67	1.95	1.41	1.74	1.91
Modulus at 300% elongation (MPa)	Before aging	2.41	4.14	4.22	5.21	4.01	3.93	4.30
	After aging	1.98	4.53	5.34	7.59	4.08	4.41	6.09
Volume loss (cm^3/1000)		0.50	0.47	0.39	0.33	0.48	0.41	0.36
Hardness (Shore A)	Before aging	34	44	47	50	39	42	47
	After aging	37	45	48	50	41	45	49
Compression set (%)		22.8	36.1	32.0	29.6	36.1	32.0	29.6
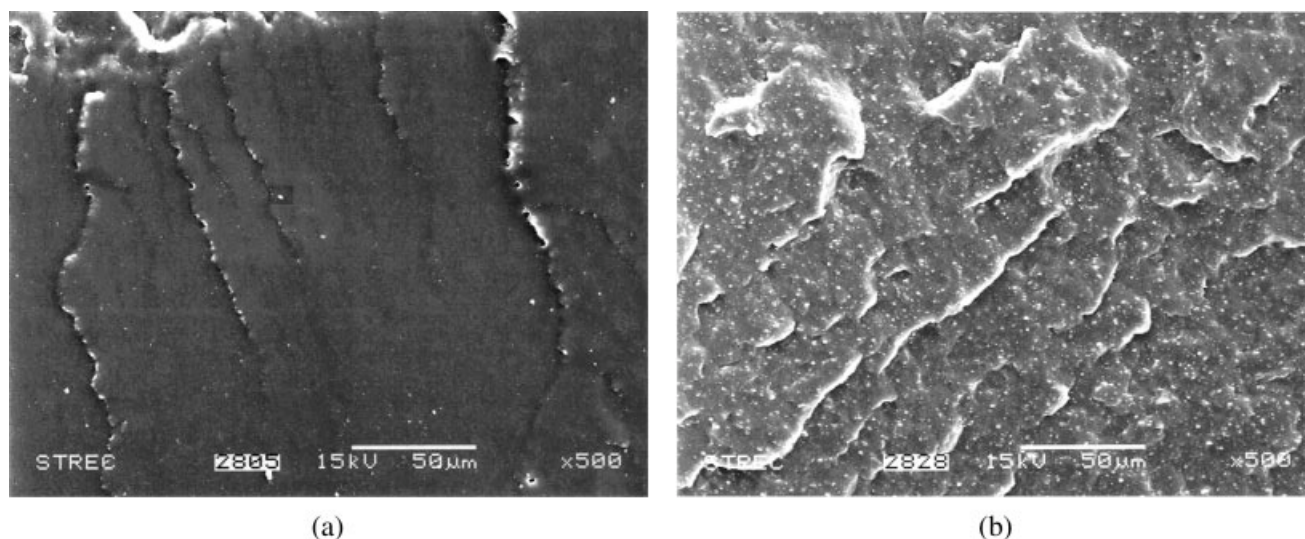
Figure 4 SEM micrographs of (a) NR and (b) NR-filled 60 phr CF novolak.

The tensile strength as well as the elongation at break of aged rubber specimens decreased. Although aging has been reported to lead to excessive crosslinks between NR molecular chains,[14] overcure occurred, and the network structure deteriorated as a result of prolonged thermal aging. The deterioration in the tensile strength and elongation may principally have been due to main-chain scission. The chain scission could be related to an oxidative reaction that was initiated by oxygen that propagated autocatalytically.[14] As the number of polysulfidic crosslinks increased, the sample became more susceptible to oxidative aging.[15] Although the tensile strength and the elongation at break of the unfilled samples dropped markedly, the reduction was less in the case of CF-resin-filled NR, especially at higher loadings. This was due to the antioxidative behavior of the CF resins. Phenolic compounds are antioxidants that can react with peroxy radicals, chain radicals, and hydroperoxide to produce inactive decomposition products.[11] The modulus at 100 and 300% elongation of the unfilled samples also decreased because of the degradation of the polymer chain. However, in the case of the CF-resin-filled samples, the modulus was improved because of excessive crosslinks as well as the pronounced thermoset characteristics of the CF resins. Aged rubbers showed higher hardness than unaged samples because of excessive crosslinks that hardened the rubber.[14]

CONCLUSIONS

CF resole and CF novolak resins were synthesized from CNSL. The optimum conditions were found for the two resins. The resins were used as reinforcing fillers in NR. The hardness, tensile strength, modulus at 100 and 300%, and abrasion resistance of the filled rubbers were enhanced compared with those of the unfilled products. Although the elongation at break and resiliency of the filled specimens were lower than those of the unfilled specimens, they improved as the amount of the fillers increased. The improvement of the mechanical properties was due to the compatibility between NR and long side chains of CF resins as well as the uniform dispersion of the filler in the matrix, as revealed by SEM. After aging, the tensile strength and the elongation at break were lower, whereas the hardness and modulus were higher. The changes in the mechanical properties with respect to the amounts of the fillers followed the same trend as those of the unaged specimens.

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