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MODIFICATION OF RUBBER BY CARDANOL-FORMALDEHYDE RESINS AND EPOXIDIZED CARDANOL

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ABSTRACT

Cardanol-formaldehyde resin (CF) and cardanol glycidylether (CGE) have been synthesized for reinforcing natural rubber (NR), a blend of NR and styrene-butadiene rubber (SBR), and nitrile-butadiene rubber (NBR). The novolac CF resin reinforced the NR, SBR, and NBR. The resolic CF is not only a reinforcing agent but also a hardener (crosslinking agent) for NBR by means of the methylol groups of CF with the CN— group of NBR. The CGE resin was synthesized by the epoxidation of cardanol by epichlorohydrin; it could be used as a reinforcing agent for NR and for crosslinking maleinized NR. The results of estimates of the physical properties of the vulcanisate, their DSC diagrams, and SEM showed the enhanced properties of the final products.

INTRODUCTION

The main component in cashew nut shell liquid is anarcadic acid. At more than 200°C, it was decarboxylated into cardanol [3]. So, cardanol could be reacted as a phenol, but there is also a long unsaturated chain of 15 C and therefore many precious properties of this compound have received attention. The phenol-formaldehyde (PE) and epoxy resin have been studied by many authors with the aim of reinforcing and modifying natural and synthetic rubbers [4, 6, 7, 8, 10, 11].

We studied here some reactions on the —OH group and aromatic nucleus of cardanol for estimating their influence on the physical properties of NR, SNR, and NBR.

EXPERIMENTAL

Cardanol was distilled 2 times at vacuum pressure of 2 ÷ 4 mm Hg at 212–218°C. CNSL consisting of 67% cardanol, 18% cardol, and 3% 2-methylcardol was analyzed by HPLC:

- Density (30°C): 0.93–0.935
- Iodine number: 245–250
- Hydroxyl number: 190–195.

Materials:

- Formaldehyde: 37%
- Epichlorohydrin 95% *t*° boiling point: 115°–118°C
- Vietnam natural rubber, smoked sheet density (g/cm^3): 0.940
- Russian CKC 30 SBR with 30% styrene content.

The molecular weights of CF and CGE were determined by the methods of Menzies and Wreight [5].

The viscosity of the masticated rubber was measured by the Kappep method. Determinations were made by DSC, TGA (TA-50 differential scanning calorimeter), and SEM (Jeol 5300 scanning electron microscope, Japan).

Synthesis of CF

This resin was condensed in the 1/1.05 molar ratio of C/F with acid or hydroxide catalysts in xylene; the water was removed by azeotropic distillation. The obtained novolac resin has a melting point of 73°–78°C and the resolic CF has a curing time, at 150°C, of 90 min.

Synthesis of Cardanol Glycidylether (CGE)

The reaction of epichlorohydrin with cardanol is shown by the IR spectrum of CGE: 1150–1200 cm^{-1}; ether linkage C—O of cardanol. The oxirane group was reversed by an opening reaction with HCl in dioxan [5]. CGE has epoxy group content of 6–6.5.

Rubber Processing

The degradation of NR, SBR, NBR was done on a two-roll mill at 70°C. For the maleinization of NR, the rubber was masticated on the roll, then maleic anhydride and benzoyl peroxide (BPO) with the former was extruded at 95°C.

Vulcanization of Rubber

The masticated compounds were vulcanized under 25 MPa pressure at 165°C for 50–90 min to sheets of 2 mm thickness. The final products were tested according to ASTM standards.

TABLE 1. Influence of CGE Content on Physical Properties of NR

CGE (phr)	Hardness (Shore A)	Abrasion resistance (cm^3/1.61 km)	Elongation at break (%)
5	50	0.41	620
10	52	0.20	610
15	58	0.16	540
20	65	0.16	504
25	65	0.25	270
30	60	0.38	223
35	54	0.50	216

RESULTS AND DISCUSSION

Modification of NR by CGE and AM

The maleinized NR was mixed with HAF-N330 carbon black 30 phr, M accelerator 2.5 phr, TMTD accelerator 0.5 phr, ZnO 5 phr, stearic acid 3 phr, and sulfur 2.5 phr. This compound was vulcanized at 160°C for 120 min at 25 MPa pressure.

The influence of CGE amounts on physical properties of final products is shown in Table 1 and the swelling capacity of the vulanizate in two solvents are shown in Table 2.

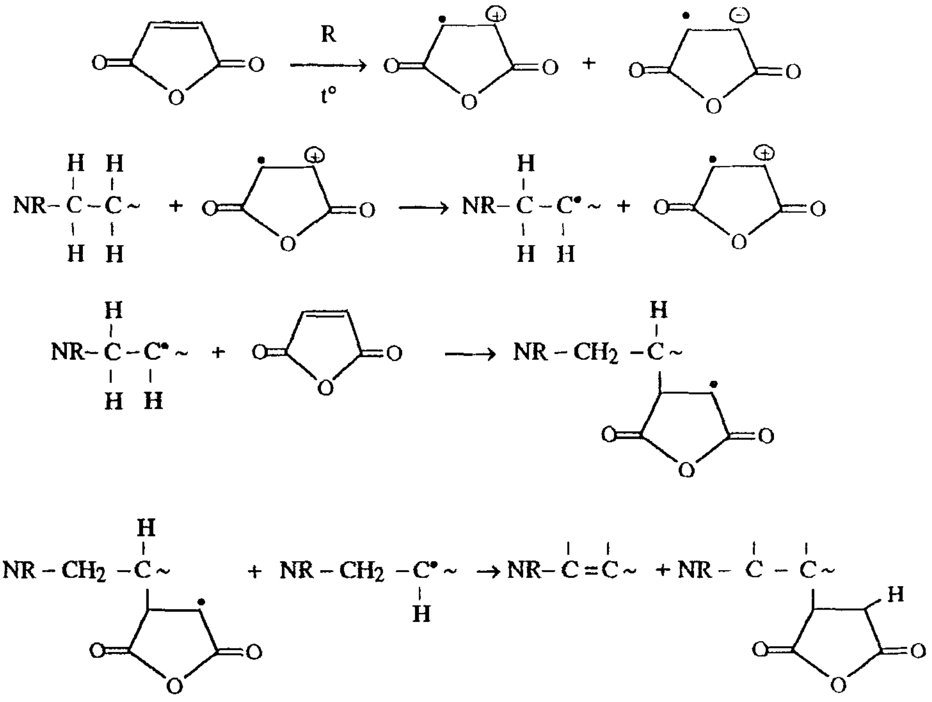
Evidently, using CGE and AM for modifying NR ameliorates the hardness, abrasion resistance, and swelling capacity of the final products. It could be explained that the CGE has taken the roles of a hardener and a softener (for good dispersal of vulcanized reagents). In the final product, a network of CGE and NR has been formed. The reaction scheme for modification of NR could be assumed to be as shown in Scheme 1. And the epoxy groups of CGE react with the maleinized rubber as shown in Scheme 2.

Influence of CF on the NR-SBR Blend

The NR and SBR blend has been investigated by many authors [1, 2]. We studied here the influence of CF to the compatibility of NR and SBR. The compound consists of ZnO 5 phr, stearic acid 3 phr, sulfur 2.5 phr, M accelerator 1.5 phr, TMTD accelerator 0.5 phr, and NR and SBR.

TABLE 2. Swelling Capacity of NR-CGE in Solvents (%)

	CGE (phr)							
Solvent	0	5	10	15	20	25	30	35
Xylene	12.5	8.5	5.3	4.5	3.8	4.0	4.8	4.1
Acetone	0.5	1.2	3.0	2.5	2.5	2.0	2.6	2.6

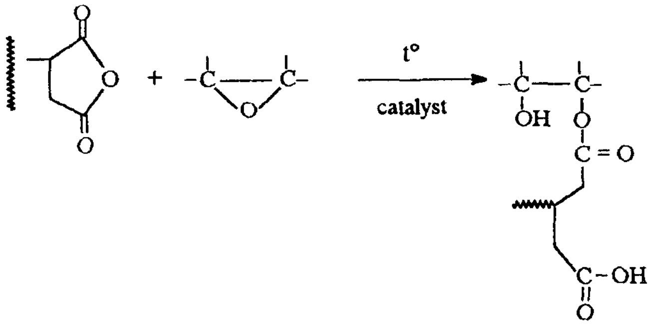


SCHEME 1.

The weight ratio of CF/urotropin is 9/1. The SBR/NR ratio is 5/95. The influence of CF on viscosity of NR-SBR blends is shown in Fig. 1.

It could be shown that the Kappep viscosity of the sample with CF is more stable than that without CF, and it could be explained that the CF has prevented the repolymerization of SBR molecules. This process has often taken place when SBR rubber is masticated; it makes it possible to easily mix all vulcanized reagents on the rollers.

The influence of different CF/urotropin quantities on the physical properties is presented in Table 3. When the proportion of CF resin to rubber is in the range of 10–25 phr, the modified products will gain the best physical properties. If this proportion is increased, the hardness and abrasion resistance of the product will be



SCHEME 2.

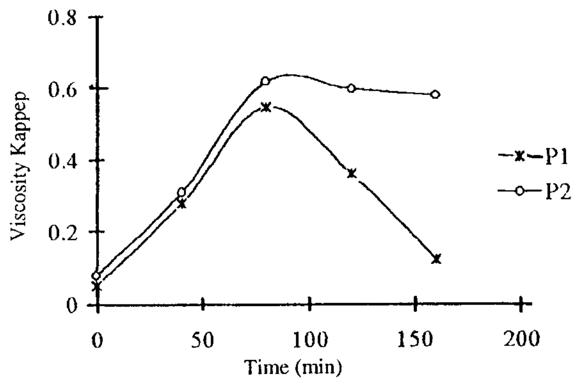


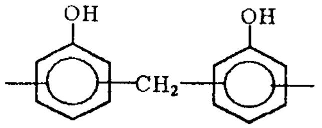
FIG. 1. Influence of CF on the Kappep viscosity. Curve 1: Kappep viscosity of NR-SBR compound without CF. Curve 2: Kappep viscosity of NR-SBR-27/3 CNSL/urotropin.

better but its elongation at break will become worse. The tensile strength of the sample with CF is 25% higher than that without CF. The influence of CF and PF on the physical properties of the materials is shown in Table 4.

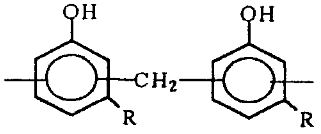
It could be considered that both PF and CSNLF resins have enhanced the physical properties of the materials, but the CF is the better enhancer.

The DSC and TGA diagrams of these two samples are shown in Fig. 2. The thermal stability of the NR-SBR blend modified by CF is a little better than that of the blend without it.

From the scanning electron micrographs (SEM), it could be seen that the HAF carbon black was well dispersed in the NR-SBR blend by CF resin [Fig. 3(a) and 3(b)]. The superiority of the CF resin is explained by its chemical structure, having a long unsaturated carbon chain, as illustrated. R is an unsaturated chain usually consisting of mixtures of $C_{15}H_{29}$, $C_{15}H_{27}$, and $C_{15}H_{25}$.



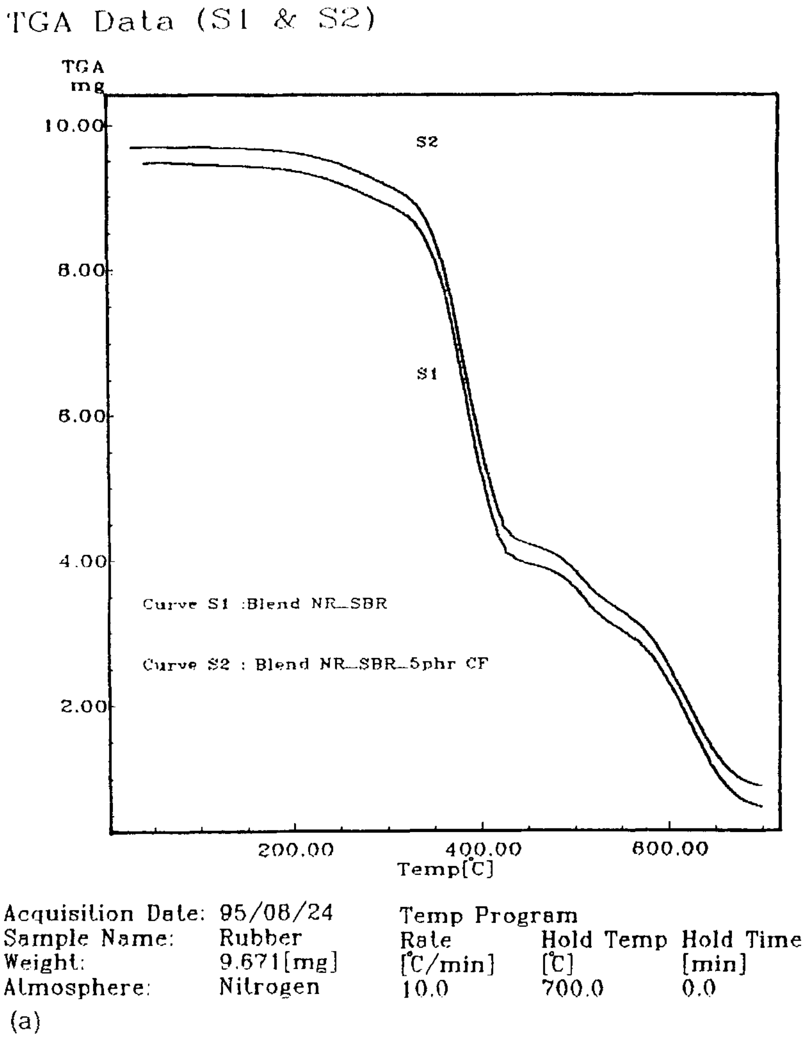
(a)



(b)

TABLE 3. Physical Properties of the NR-SBR-CF Material

	CF/urotropin						
Property	0	9/1	18/2	17/3	36/4	45/5	54/6
Hardness (Shore A)	68	75	78	84	84	87	88
Tensile strength (MPa)	73	8.4	9.8	9.5	8.8	8.1	8.0
Abrasion resistance (cm^3/1.61 km)	0.72	0.45	0.31	0.31	0.22	0.32	0.35
Elongation at break (%)	890	790	650	650	620	580	510



Acquisition Date: 95/08/24
Sample Name: Rubber
Weight: 9.671[mg]
Atmosphere: Nitrogen

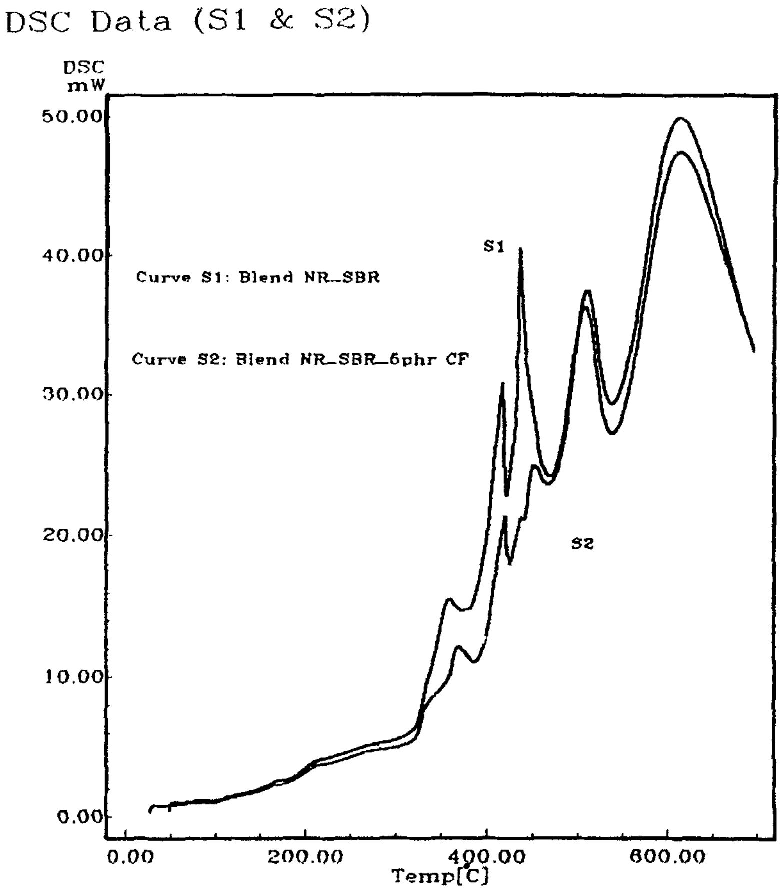
Temp Program

Rate [°C/min]	Hold Temp [°C]	Hold Time [min]
10.0	700.0	0.0

FIG. 2. (a) TGA diagram of blends NR-SBR and NR-SBR-CF. (b) DSC diagram of blends NR-SBR and NR-SBR-CF.

TABLE 4. Physical Properties of the NR-SBR-CF and NR-SDR-PF Materials

	HAF carbon black 50 phr	HAF carbon black 25 phr + CF 25 phr	HAF carbon black 25 phr + PF 25 phr
Hardness (Shore A)	69	81	82
Tensile strength (MPa)	7.5	10.4	8.8
Abrasion resistance (cm^3/1.61 km)	0.71	0.21	0.25



Acquisition Date:	95/08/24	Temp Program		
Sample Name:	Rubber	Rate	Hold Temp	Hold Time
Weight:	9.700[mg]	[C/min]	[C]	[min]
Atmosphere:	Nitrogen	10.0	700.0	0.0

(b)

FIG. 2. Continued

TABLE 5. Physical Properties of the NR-SBR-CF and NR-SBR-PF Materials

	Hardness (Shore A)	Tensile strength (MPa)	Abrasion resistance (cm^3/1.6 km)	Elongation at break (%)	Swelling capacity in benzene (%) after 24 h
NBR-PF	0.82	33.2	0.41	6.20	5.6 ÷ 6.2
NBR-CF	0.78	35.8	0.35	6.50	5.1 ÷ 5.7

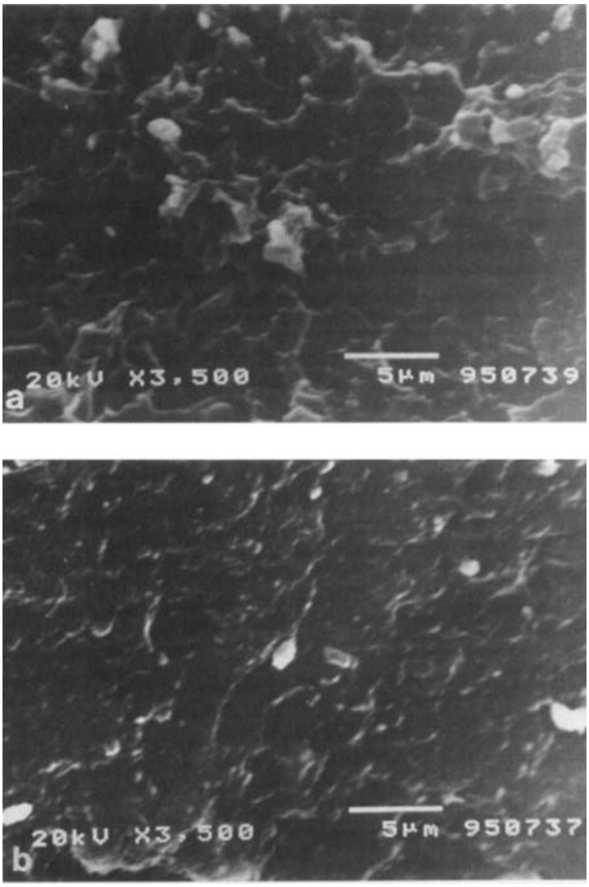
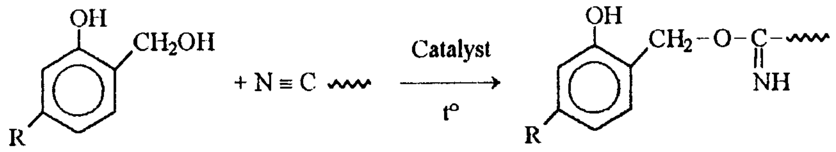


FIG. 3. (a) SEM of blend NR-SBR-CF. (b) SEM of blend NR-SBR-CF.

TABLE 6. Influence of Resol CF on the Physical Properties of NBR

		CF resol					
Property	S: 2.5	5	10	15	20	25	30
Hardness (Shore A)	70	22	35	40	48	52	68
Tensile strength (MPa)	31.5	4.2	8.7	15.1	18.0	21.2	20.5
Elongation at break (%)	680	250	458	420	412	345	280



SCHEME 3.

The CF resin takes roles as a hardener and a softener, which makes the vulcanized reagents disperse well into the rubber. It then takes some part in the vulcanization of the rubber compound by means of their functional groups and diene linkages, so that the physical properties of these blends are ameliorated.

Influence of CF on the NBR Compound

The CF resin was synthesized in two kinds of novolac and resol resins. The compound was as in [3-2] paragraph. The CF (or PF)/NBR ratio is 9/100.

HMTA was used for curing the CF and PF resins, with the weight ratio CF/HMTA = 9/1 and PF/HMTA = 9/1. The physical properties of NBR with PF and CF resin are shown in Table 5.

It could be considered that the novolac CF is a better reinforcing agent than PE, but the resolic CF also gives considerable reinforcement. Table 6 shows the influence of resolic CF on NBR.

Evidently, without S and with $SnCl_2$ as a catalyst, the vulcanizations of NBR has also taken place. This could be explained by the dispersal of the polymerized resolic CF of high molecular weight in the NBR, along with the spontaneous thermosetting of the 2 methylol groups of resolic CF with the nitrile group of NBR [9]. It could be assumed to proceed as illustrated in Scheme 3.

When the complex novolac and resolic CF was used for the formulation, it could be seen from the SEM that the dispersion of vulcanized reagents in this system is better than that of novolac CF.

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