

Thermal Behavior of Elastomer–Resin Mixtures Used as Friction Materials

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ABSTRACT: This study looks at the thermal behavior of mixtures of nitrile-butadiene rubber (NBR) with a resol or a novolac resin. When heated in the 200–300°C range, NBR became hard and insoluble because of exothermic curing and cyclizing chain reactions involving the double bonds of its butadiene units and the nitrile groups of its acrylonitrile units. The NBR proved to be compatible with the novolac but not the resol. Heating increased the modulus of elasticity of the mixtures, which was due to crosslinking of the resin and the rubber. Preliminary linking of the resin resulted in phase separation in the novolac and prevented curing of the rubber when the mixture was heated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1346–1351, 2001

Key words: thermal behavior; elastomer; nitrile-butadiene rubber; resol resin; novolac resin

INTRODUCTION

Motor vehicle brakes are lined with a friction material composed of fillers, metals, lubricants, fibers, and binders.^{1,2} This article examines the phenolic resin and synthetic rubber binders that form the organic component of the material. Rubbers [mainly nitrile-butadiene (NBR) and styrene-butadiene (SBR)^{3,4}] make the material elastic, while resins confer compactness and wear resistance.^{5,6} When the raw materials are mixed, the resin dissolves and is uniformly distributed. During the subsequent molding and oven curing stages of the manufacturing process it crosslinks to form a compact brake pad.

The main drawback of using organic material for the production of brake pads is its low thermal

stability at the 300–500°C temperatures reached during braking. This article examines the effects of heating on the properties of two rubber–resin mixtures.

EXPERIMENTAL

Materials

The NBR that was used was Krynac 34.35 (Bayer). Its acrylonitrile content was 33 wt %, and it was completely soluble in benzene. In the copolymer the butadiene units were 1,4-trans and 1,2.

Samples of two phenolic resins were obtained from FERS (Barcelona, Spain): a novolac, which was devoid of crosslinking agent with a low free phenol content, and a resol. Hexamethylene tetramine (HEXA) from FERS was used as the crosslinking agent for the novolac.

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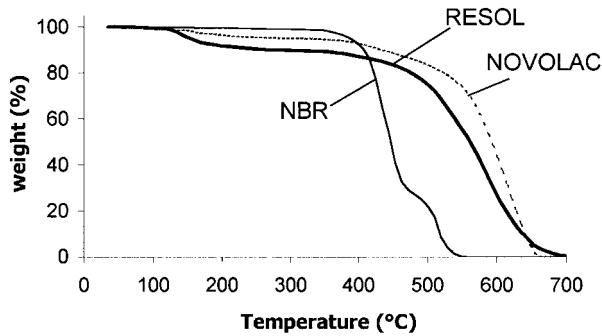


Figure 1 TGA curves of NBR, resol, and novolac heated in air at 10°C/min.

Thermogravimetric Analysis (TGA)

A Mettler TGA 50 thermobalance with a ceramic sample holder was employed at a heating rate of 10°C/min and an air or nitrogen flow rate of 200 mL/min.

Differential Scanning Calorimetry (DSC)

A Mettler 821 heat flow calorimeter fitted with covered steel sample pans was employed at a heating rate of 10°C/min and an air or nitrogen flow rate of 200 mL/min. An identical empty pan was used as the standard.

Dynamic Mechanical Thermal Analysis (DMTA)

A Metravib R.D.S. viscoanalyzer was used. The NBR and mixture cubes with 1-cm sides were fixed with acrylic glue between the two pans of the sample holder and subjected to tension-compression stress at the following parameter values: 1×10^{-6} m stress amplitude, 200 mL/min air flow rate, 10-min pauses between temperatures, and a 52-Hz frequency.

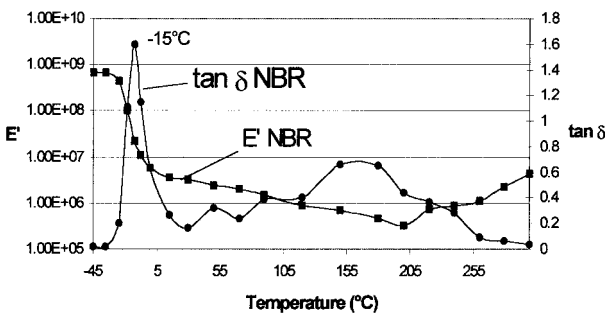


Figure 2 The viscoelastic properties of NBR at a frequency of 52 Hz.

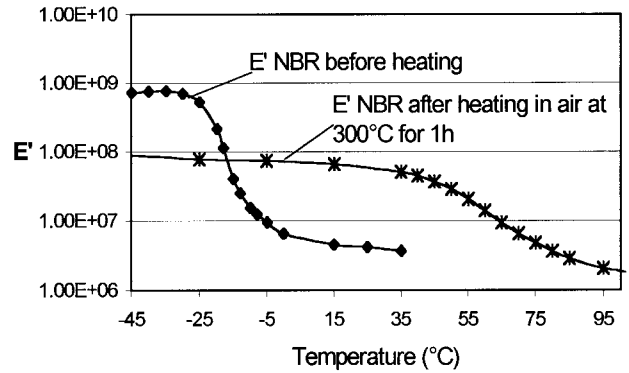


Figure 3 The modulus of elasticity (E') of NBR before and after heating in air at 300°C for 1 h at a frequency of 52 Hz.

The DMTA plots showed the patterns of the modulus of elasticity ($\log E'$) and loss factor ($\tan \delta = E''/E'$) as a function of the temperature.

IR Spectroscopy

In view of the characteristics of NBR, we decided to carry out attenuated total reflectance⁹ spectroscopy of approximately $0.5 \times 2 \times 2$ cm samples before and after heating. A Perkin-Elmer Spectrum One Spectrophotometer and Multiscope System with a germanium crystal were used.

Mixing

A Bambury internal mixer with a water cooling jacket was used to obtain a mixture of 500 g of NBR and 500 g of resin. This mixture gave a clearer idea of the effects of each component on its behavior.

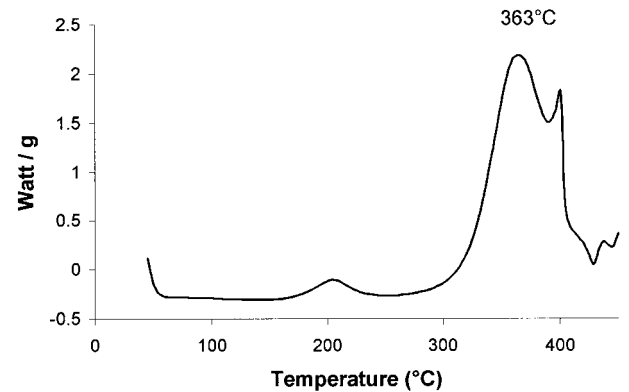


Figure 4 A DSC plot of NBR heated in air at 10°C/min.

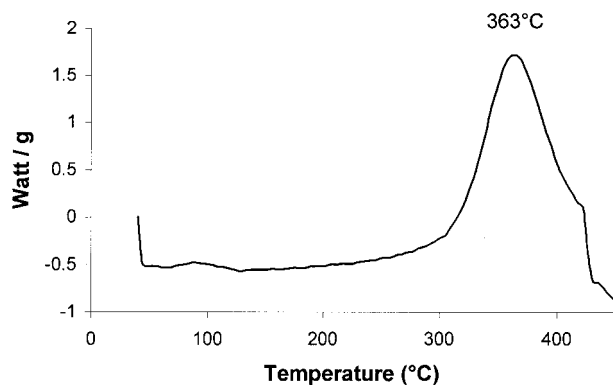


Figure 5 A DSC plot of NBR heated in nitrogen at 10°C/min.

The rubber was masticated for about 5 min. The resin was then introduced (with HEXA for the novolac) and mixed in for another 5 min. The cooling jacket ensured that the mixtures were kept at less than 70°C to prevent crosslinking of the resin in the mixer.

RESULTS AND DISCUSSION

The behavior of the individually heated rubber and resin was also studied.

TGA Comparison

A comparison of the TGA curves for NBR, the novolac, and the resin in air (Fig. 1) showed that in the 200–500°C range the NBR underwent the greatest transformation. Thus, the thermal degradation and weight loss that occurred in the rubber–resin mixtures in this range was mainly due to the degradation of the rubber that began at about 350°C.

Rubber Curing

Two points emerged from the DTMA data for NBR (Fig. 2). There was a steep drop in the E' corresponding to a loss factor peak at -15°C attributable to the glass transition, while the increase in E' above 200°C indicated hardening. This was probably attributable to a heat-induced change in the polymer structure, because the glass-transition temperature of NBR after heating at 300°C for 1 h was 60°C compared to -15°C for the raw rubber (Fig. 3).

The DSC exothermic peak that appeared when NBR was heated in air (Fig. 4) and nitrogen (Fig. 5) indicated that the rubber transformations responsible for hardening were due to exothermic reactions in the polymer that did not depend on oxygen.

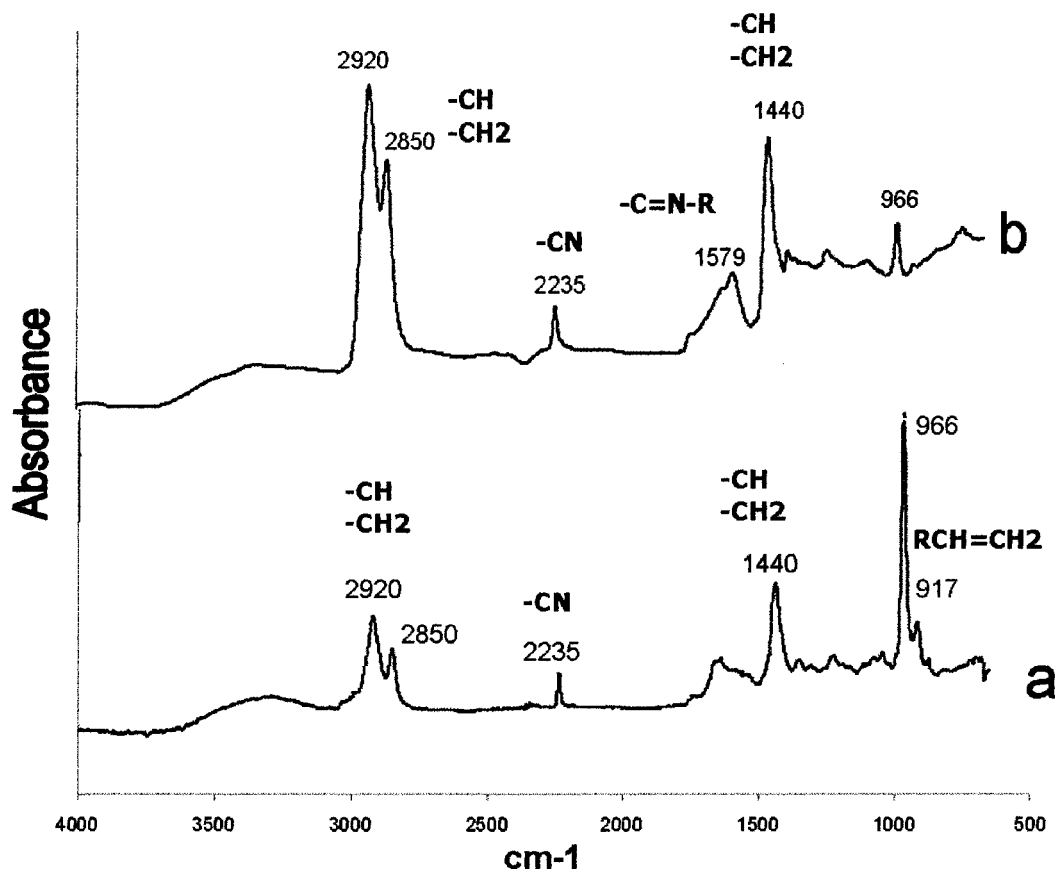


Figure 6 The attenuated total reflectance spectra of raw NBR (spectrum a) and NBR after heating at 310°C for 2 h in an inert atmosphere (spectrum b).

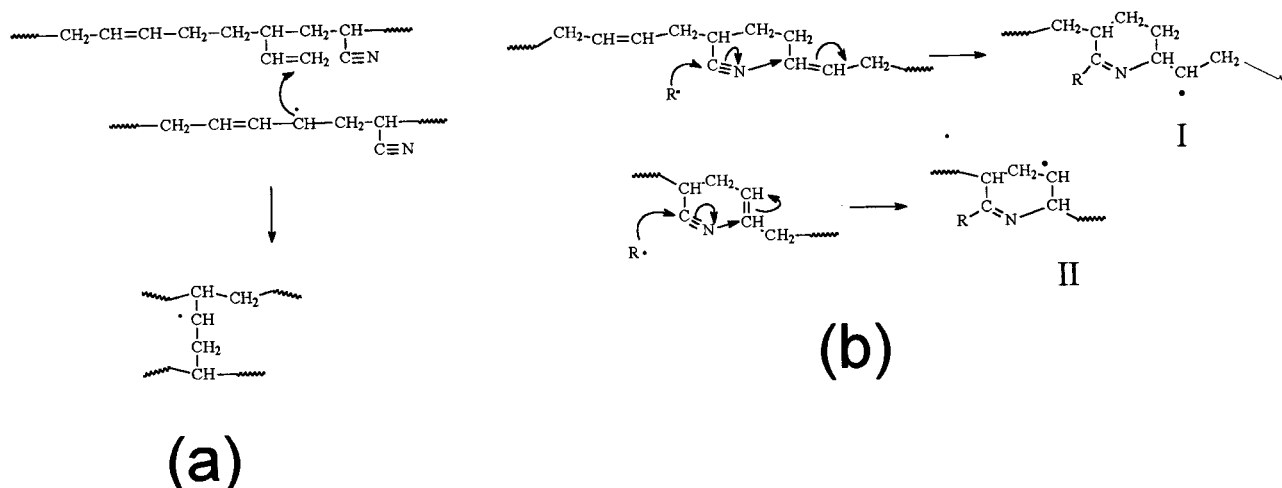


Figure 7 The suggested hardening mechanisms: (a) the addition of a radical to a vinyl group and (b) the cyclization promoted by the CN groups.

The investigation of the mechanisms of these reactions by comparing and interpreting^{10,11} the spectra of raw NBR [Fig. 6(a)] and NBR heated at 310°C in an inert atmosphere for 2 h [Fig. 6(b)] showed diminution of the intensity of the peak for the nitrile groups at 2235 cm^{-1} and that of the peak at 966 cm^{-1} corresponding to vibrations due to deformation of the C—H bond in *trans*-alkenes. These decreases were related to the peak at 2920 cm^{-1} that is typical of the vibrations of C—H stretching in saturated structures. The investigation also showed the disappearance of the peak at 917 cm^{-1} , which is typical of the vinyl structure of the 1,2-butadiene unit, and the appearance of a new peak at 1579 cm^{-1} , which was attributable to imines.

These observations and the literature data on polyacrylonitrile¹³ and polybutadiene¹⁴ degradation in the 200–500°C range were used to postulate the two mechanisms illustrated in Figure 7. The mechanism in Figure 7(a) envisages the addition of a radical, which is formed in a chain due to cleavage of a C—H bond, to a vinyl double bond of the 1,2-butadiene unit. This addition leads to the formation of a bond between the two chains and hence crosslinking as in polybutadiene.¹⁴ The mechanism in Figure 7(b), on the other hand, envisages intramolecular cyclization by radical initiated addition between nitrile and the carbon-carbon double bond of adjacent acrylonitrile-butadiene repeating units of NBR. This mechanism is the equivalent of nitrile-nitrile addition occurring on heating polyacrylonitrile.¹³ Radicals I and II, which are created by the intramolecular addi-

tion, can further contribute to crosslinking by addition to vinyl double bonds or other nitrile groups.

NBR-Resin Mixtures

Mixtures of NBR plus resol and NBR plus novolac were studied. The most interesting data were provided by DMTA. An examination of the plot of the E' of NBR and NBR plus resol as a function of temperature [Fig. 8(a)] showed the variation in E' corresponding to the glass-transition temperature (T_g) of NBR (–15°C), whereas the transition temperature of the resol (about 50°C) was indicated by a small loss factor peak [Fig. 8(b)]. The fact that the two polymers retained their T_g showed that they were incompatible (i.e., immiscible). Their miscibility, in fact, would require the negative enthalpy of mixing $[\Delta H_{\text{mix}} = \frac{1}{2}(H_{11} + H_{22}) - H_{12}]$ ^{15,16} that occurs when H_{12} , the NBR-resol interaction term, has a greater absolute value than the NBR-NBR or the resol-resol interaction terms H_{11} and H_{22} . Incompatibility between the polymers occurs because resol contains many polar groups (CH_2OH and OH) and NBR has few (CN). Resol-resol interactions therefore take precedence over NBR-resol interactions.

The NBR plus novolac mixture, on the other hand, displayed a single T_g at 40°C [Fig. 9(a)], which was midway between those of the individual polymers [Fig. 9(b), novolac T_g by DSC = 66°C] and indicative of their compatibility. Because novolac contains fewer polar groups than

resol, it may be presumed to interact more readily with NBR.

The increase in E' above about 200°C in both mixtures showed curing of the rubber in the presence of the resin.

The two mixtures were also slowly heated to 200°C for 4 h to study the effect of gradual crosslinking of the resin on their properties.

In both mixtures the E' above about 55°C was higher than that of the untreated mixtures because of crosslinking, which also shifted the T_g of the resol from 55°C to higher temperatures [Fig. 8(b)]. In this case the T_g of the rubber was still at -5°C, from which we deduced curing above 200°C from the increase in E' as for the untreated mixture [Fig. 8(a)].

In the novolac mixture, after treatment the NBR T_g was at -15°C, which was not observed before the treatment [Fig. 9(a,b)], whereas the T_g at 40°C, which was typical of the untreated mixture, disappeared. This showed that crosslinking of the resin resulted in unmixing of the mixture. It also seemed that curing of the NBR in this mixture was difficult after crosslinking of the resin because the increase of E' after 200°C was negligible [Fig. 9(a)].

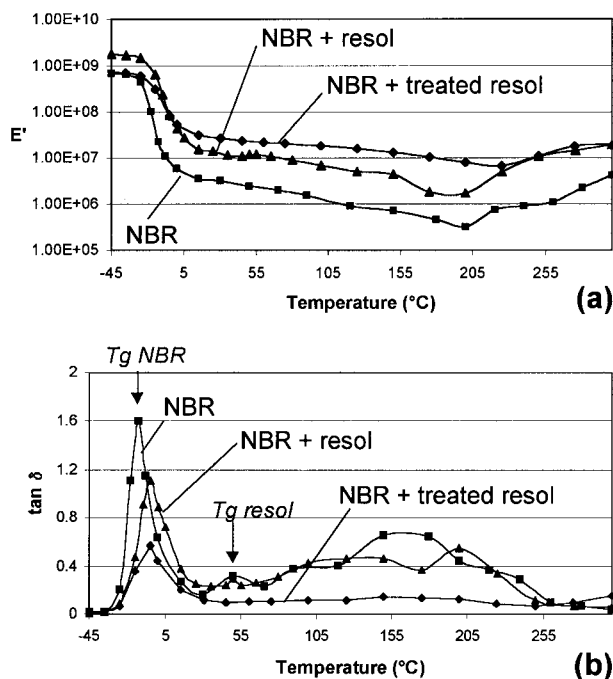


Figure 8 (a) The modulus of elasticity (E') of NBR, NBR plus resol, and NBR plus treated resol after heating at 200°C for 4 h. (b) The loss factor of NBR, NBR plus resol, and NBR plus treated resol after heating at 200°C for 4 h.

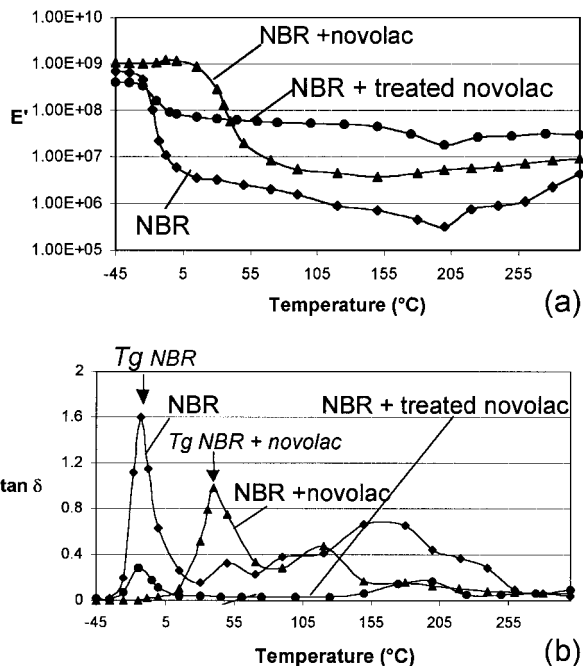


Figure 9 (a) The modulus of elasticity (E') of NBR, NBR plus novolac, and NBR plus treated novolac after heating at 200°C for 4 h. (b) The loss factor of NBR, NBR plus novolac, and NBR plus treated novolac after heating at 200°C for 4 h.

CONCLUSIONS

When heated in the 200–300°C range, NBR became hard and insoluble as the result of exothermic curing and cyclization reactions involving the double bonds of its butadiene units and the nitrile groups of its acrylonitrile units.

Combination of NBR with a resol and with a novolac gave an immiscible mixture and a miscible mixture, respectively. The compatibility of the novolac mixture was reduced when it was heated to temperatures that allowed crosslinking of the resin.

Crosslinking increased the rigidity of the material, particularly in the case of the novolac mixture, although here it also provoked unmixing of the mixture and prevented curing of the rubber.

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