

Dynamically Vulcanized Blends of Oil-Resistant Elastomers with HNBR

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ABSTRACT: Dynamic vulcanizates were produced from hydrogenated nitrile rubber (HNBR) and three different oil-resistant elastomers. These are polychloroprene (CR), epoxidized natural rubber (EIR), and carboxylated nitrile rubber (XNBR). These elastomers are dispersed and crosslinked during mixing with HNBR. These dynamic vulcanizates all have an HNBR continuous phase. The HNBR matrix is subsequently crosslinked. Stress-strain measurements in tension and tear resistance were measured on the

crosslinked dynamic vulcanizates as well as on cured HNBR, CR, EIR, and XNBR. Measurements were also made following hot air and oil aging. Following aging, the dynamic vulcanizates retain a significant amount of their properties due to the presence of the HNBR matrix. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 2–5, 2005

Key words: vulcanization; blends; rubber

INTRODUCTION

Butadiene-acrylonitrile rubber (NBR) was invented by Konrad and Tschunkur¹ of the I.G. Farbenindustrie in 1929. It was commercialized in 1934 as an oil-resistant rubber and proved to be a major improvement over natural rubber, in “under the hood” and similar applications because of its lack of ozone resistance. As early as the late 1930s, it was blended with poly(vinyl chloride) and other polymers^{2,3} to obtain improvement in aging.

In the 1970s, there was an extended effort to hydrogenate butadiene acrylonitrile copolymer.^{4,5} This continued in to the next decade.^{6–9} Subsequently, Bayer AG brought their Therban® hydrogenated NBR or HNBR into the market and Nippon Zeon made Zetpol® HNBR commercial. Various investigators have studied the material properties and thermal transitions of these materials.^{10–18}

HNBR, while having high performance characteristics, is an expensive material. This has led to the investigation of its blends with other elastomers.¹⁹ Generally, HNBR is immiscible with most commercial elastomers. It is, however, miscible with certain chlorinated polyethylenes and poly(vinyl chloride). In the present paper we seek to develop a family of dynamically vulcanized blends in which oil-resistant elastomers are dispersed as vulcanized particles in an HNBR matrix. This type of product should retain its

superior oil-resistance properties and much of its aging resistance at lower material cost.

EXPERIMENTAL

Materials

The elastomers chosen in this study were a 36% acrylonitrile HNBR (Zetpol 2030L from Zeon Chemical), a polychloroprene (CR) (Bayprene 121 from Bayer), an epoxidized polyisoprene (EIR) (Epoxyplene-50 from Guthrie Latex), and a carboxylated NBR (XNBR) (Nipol DN120) from Zeon Chemical).

Recipes

Special recipes that would cure one of the elastomers while being mixed but not the HNBR were used in mixing. These recipes are contained in Tables I–III.

Mixing and dynamic vulcanization

The various blends were prepared in a Brabender Plasticorder by simultaneously introducing both elastomers into the mixer in the desired proportions (25/75, 50/50, and 75/25).

For the CR and HNBR dynamically vulcanized systems, we introduced MgO, ZnO, and stearic acid after 3 min of mixing at 50°C. The recipe is in Table I. The mixing was continued for another 6 min at 150°C, during which period the dynamic vulcanization of the CR occurred. After the 9-min mixing cycle, we removed the rubber and placed it on a two-roll mill where sulfur and accelerators were added. The curing

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TABLE I
Recipe Used for CR/HNBR Dynamic Vulcanizates

Elastomers	100
CR Curatives	
MgO	2
ZnO	5
Stearic Acid	1
HNBR Curatives	
Sulfur	0.5
Tetramethylthiuran disulfide (TMTD)	2
2 Mercaptobenzothiazole (MBT)	0.5

times for the HNBR were subsequently determined with a Monsanto oscillating disc rheometer. Curing of the HNBR was carried out in a compression molding press.

A similar procedure was used for the EIR/HNBR dynamically vulcanized blends. The recipe is shown in Table II. For this system we introduced EIR and HNBR at 140°C. We introduced 1% maleic anhydride into the mixture, which preferentially reacts with the EIR. After 2 min of further mixing we introduced the ZnO and stearic acid, which crosslinks the maleated EIR. The EIR then disperses in the HNBR matrix. Mixing was continued for 11 min. When the 13 min elapsed, the rubber blend was then removed from the internal mixer and the sulfur and HNBR curatives were added on the two-roll mill. It was then vulcanized in a compression molding press.

The XNBR/HNBR dynamically vulcanized blends were also prepared in the same internal mixer. The recipes are shown in Table III. They were mixed at 60 rpm for 9 min at 50°C. MgO and stearic acid curatives were then added. These crosslink the XNBR and cause it to become dispersed in the HNBR matrix. The dynamically vulcanized blends were subsequently removed from the internal mixer and sulfur and TMTD and MBT were added on the two-roll mill. Vulcanizates was carried out in a compression molding press.

Scanning electron microscopy

The morphology of the dynamically vulcanized blends was investigated using scanning electron mi-

TABLE II
Recipe Used for EIR/HNBR Dynamic Vulcanizates

Elastomers	100
EIR curatives	
Maleic Anhydride	1
ZnO	5
Stearic Acid	1
HNBR curatives	
Sulfur	0.5
TMTD	2.0
MBT	0.5

TABLE III
Recipe Used for XNBR/HNBR Dynamic Vulcanizates

Elastomers	100
XNBR Curatives	
MgO	5.0
Stearic Acid	2.0
HNBR	
Curatives	
Sulfur	0.5
TMTD	2.0
MBT	0.5

croscopy (SEM). A Hitachi S-250 instrument was used. Fracture surfaces were prepared in liquid nitrogen. OsO₄, which reacts with double bonds, was used as a staining agent for a number of the blends.

Mechanical testing

The dynamically vulcanized blends were compression molded and the HNBR phase was crosslinked in a Wabash compression molding press at 160°C.

Tensile testing was carried in a Flexsys tensile tester at room temperature at a crosshead speed of 500 mm/min.

Tear strength measurements were carried out with a trouser specimen according to ASTM D624.

Aging in air

The superior aging characteristics of HNBR relative to NBR is its primary advantage. Blends of HNBR with diene rubbers would be expected to be inferior to HNBR. Dumbbell and trouser specimens were placed in a circulating air oven at 150°C for various periods of time, generally 2 to 4 days. The mechanical properties were then retested according to ASTM D573.

Aging in oil

HNBR and the blends described in this paper are intended to be used in oil environments. We investigated the effect of heated IRM-903 (formerly ASTM standard oil-3) oil at 100°C on the mechanical properties according to ASTM D471. The aging time in the oil was 72 h.

RESULTS AND DISCUSSION

Polychloroprene–HNBR blends

SEM photomicrographs of the blend phase morphology for the various dynamically vulcanized blends were obtained. These indicate that the CR is dispersed in the HNBR matrix. These show that, for the 25/75 CR/HNBR blend, the dispersed phase size of the CR was about 1.85 μm . For the 50/50 blend the dispersed

phase size of the CR was about 2 μm . The dispersed phase size in the 75/25 dynamically vulcanized blend was difficult to detect but seemed larger.

Engineering stress–strain curves of CR, HNBR, and the dynamically vulcanized 25/75, 50/50, and 75/25 blends were determined. The elongations to break of the CR and HNBR vulcanizates were about 600 and 320%, respectively. The values for the dynamically vulcanized blends were 180–350%, with the smallest value being for the 75/25 blend. For the 25/75 and 50/50 blends the elongations to break were similar. The tensile strengths were in the range of 5 to 8 MPa for all of the blends. The tear strengths were in the range of 18 to 31 KN/m. They were about 18 KN/m for the HNBR and the 25/75 blend. They were higher for the 50/50 and 75/25 blends as well as for the CR.

The influence of aging was studied primarily using elongation to break and tensile strength. The HNBR vulcanizate had an elongation to break of 400% and after 2 days at 150°C in an air oven the value was about the same. After 4 days, the elongation to break had been reduced to about 200%. For the CR vulcanizate the value was reduced from 600% (initial) to 40% (2 days) to 0% (4 days). For the CR/HNBR 25/75 blend the value changed from 350% (initial) to 120% (2 days) to 50% (4 days). For the 50/50 CR/HNBR blend, the value decreased from 350% (initial) to 40% (2 days) and 0% (4 days). The 75/25 CR/HNBR was reduced from 190% (initial) decreasing to 40% after 2 days and to 0% after 4 days. The tensile strength for the HNBR was decreased from about 5 MPa (initial) to 2 MPa (2 or 4 days). For the CR vulcanizate, the tensile strength was reduced from 7 MPa (initial) to 3.5 (2 days) to 0 (4 days). The 75/25 blend had values of 6 MPa (initial), 3 MPa (2 days), and 5.5 MPa (4 days). For the 50/50 dynamically vulcanized blend the tensile strength was reduced from 8 to 32 MPa (2 days) and was 6.5 MPa after 4 days. The tensile strength of the 25/75 CR/HNBR blend was 6 MPa after 2 days and 5 MPa after 4 days.

Oil aging experiments for 3 days at 100°C were also carried out. The elongation to break of HNBR decreased from 350 to 200%. For the 25/75 CR/HNBR the value changed from 320 to 220%. At 50/50 the decrease was from 350 to 250%. However, for 75/25 CR/HNBR the value remained unchanged at 220%. The tensile strength of HNBR was reduced by oil aging from 5 to 4 MPa and for the CR from 7 to 1.5 MPa. At 75/25 CR/HNBR the value of 6 MPa was virtually unchanged at 5.5 MPa. At 50/50 the value of 9 MPa was reduced to 5 MPa. For the 25/75 blend the value was reduced from 5 to 4MPa.

EIR–HNBR blends

SEM photomicrographs of the blend phase morphology show the EIR rubber dispersed in the HNBR

matrix. For the 25/75 EIR/HNBR blend the dispersed phase size is about 1 μm . The EIR dispersed phase becomes coarser with increasing concentration.

Engineering stress–strain curves for EIR, HNBR, and the blends were determined. The HNBR vulcanizate has an elongation to break of 320%. The 25/75 50/50 and 75/25 EIR/HNBR dynamically vulcanized blends have values of 250, 300, and 250%, respectively. The tensile strengths for the HNBR and the 25/75, 50/50, and 75/25 dynamically vulcanized blends have values of 5.5, 4, and 2.8 MPa.

For the 150°C 2-day air oven-aged HNBR and the 25/75, 50/50, and 75/25 EIR dynamically vulcanized blends the elongation to break decreases from 320 to 300%, 260 to 75%, and 250 to 25%. The EIR was reduced to 75%. The tensile strengths of the three blends generally showed increases.

For the 3-day oil aging experiment at 100°C, the elongation to break of the HNBR decreased from 350 to 200%. For the 25/75 EIR/HBR the value decreased from 300 to 200% and for the 50/50 it decreased from 250 to 150%. For the 75/25 composition, the value changed from 250 to 180%.

XNBR–HNBR blends

SEM photomicrographs were made of the blend phase morphology. Detection is difficult. These suggested that the XNBR were dispersed in the HNBR matrix.

Engineering stress–strain curves were obtained for the cured dynamically vulcanized blends as well as the XNBR and HNBR. The tensile strengths of the 50/50 and 25/75 blends were about 10 MPa. The elongations to break for these were 670 and 500%.

We air oven aged the samples for 2 days and then determined engineering stress–strain behavior. The 50/50 dynamically vulcanized blend elongation to break was reduced from 670 to 70% and that for the 25/75 blend was reduced from 500 to 200%. The HNBR itself was reduced from 430 to 370% and the XNBR was reduced from 700% to essentially 0.

For the 3-day oil-aging experiments the elongation to break of the 25/75 blend was reduced from 500 to 400% and that of the 50/50 blend from 670 to about 500%.

CONCLUSION

We described in this paper the development of dynamically vulcanized blends of HNBR with various oil-resistant elastomers including polychloroprene (CR), epoxidized natural rubber (EIR), and carboxylated nitrile (XNBR). Each of these was dispersed in the HNBR matrix. We considered the mechanical performance and the air and oil aging of the dynamically vulcanized blends.

For the unaged blends, the mechanical properties were similar to those of the HNBR vulcanizates. For the air and oil aged samples, the 25/75 CR/HNBR dynamically vulcanized blends performed the best and the 75/25 performed the worse. Generally, the dynamically vulcanized blends held up better under oil aging than under air aging.

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