

Effects of Hygrothermally Decomposed Polyurethane on the Curing and Mechanical Properties of Carbon Black-Filled Epoxidized Natural Rubber Vulcanizates

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ABSTRACT: Hygrothermally decomposed polyurethane (HD-PUR) was mixed up to 20 phr in epoxidized natural rubber (with 50 mol % epoxidation; ENR50) recipes, and the curing and mechanical behaviors were studied. Mechanical testing of the ENR50/HD-PUR vulcanizates determined the tensile, tear, compression-set, hardness, abrasion, hysteresis, and resilience properties. No significant changes were observed in the tensile properties with the incorporation of HD-PUR. The ENR50 compounds showed an increase in compression set with increasing HD-PUR content. Rubbers cured by a semi-efficient vulcanization system gave the best overall performance. A further improvement in curing and mechanical properties was achieved by the carbon black grade N330 being replaced with a more active grade (N375). © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2265–2276, 2002

Key words: epoxidized natural rubber (ENR); poly(ester urethane) (PUR); hygrothermally decomposed poly(ester urethane); rubber vulcanization; rubber characteristics; recycling

INTRODUCTION

Polyurethane (PUR) is known as one of the most versatile polymers because it can be made available in different forms, including flexible, semi-rigid, and rigid products, by the selection of suitable polyol and polyisocyanate components. The chemistry of PUR formation is well documented in the literature.¹ Because of its versatile me-

chanical, chemical, and thermal properties, PUR has found many applications in various fields. PUR is widely used in the production of shoe soles and automotive parts, with a consumption of several million tons per year. The waste generated from the manufacturing process (2–10%) and represented by postconsumer products is enormous.² The high disposal costs and ever decreasing availability of landfills, combined with increasing environmental concerns and legislation, have resulted in significant pressure to manage the PUR waste. A further challenge is to find a cost-efficient reuse for PUR processing waste, especially for that produced by the footwear industry.²

Several methods have been developed to recycle PUR scrap.^{3,4} These include physical (e.g., grinding and compression molding, bonding by

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adhesives and latex) and chemical recycling processes (e.g., solvolysis, feedstock recycling, energy recovery).

An earlier study by Sombatsompop and Sims⁵ revealed that the mechanical properties of natural rubber (NR) compounds can be varied by the incorporation of both carbon black and pulverized flexible PUR foam particles. For further diversification of the options available for PUR recycling, hygrothermally decomposed polyurethane (HD-PUR) has been produced on the premise that it may be a very suitable polymeric ingredient in rubber recipes. This idea was triggered by the fact that milled PUR is often used as a polymeric filler in rubber compounds.⁵ It is well known that crosslinked PUR can be easily decomposed hygrothermally into very versatile products.^{6,7} The appearance of related products extends from rubbery substances to highly viscous fluids. We reported earlier on the applicability of HD-PUR to NR and nitrile rubber (NBR) recipes.⁸ Increasing the HD-PUR content in NR resulted in a moderate increase in tensile and tear properties. In addition, both NR and NBR stocks showed an increase in compression set with increasing HD-PUR content. Because HD-PUR is rich in primary amine groups, it can be used as a crosslinking agent and a toughener in epoxy resins.^{6,7,9}

This study was aimed at investigating the effects of the HD-PUR type, HD-PUR content, vulcanization system, and carbon black type on the curing and mechanical properties of a relatively new type of elastomer, epoxidized natural rubber (ENR). Note that the epoxidation of NR produces a random copolymer between isoprene and epoxidized isoprene units. ENR possesses attractive properties, such as good oil resistance, reduced air permeability, high damping, and good wet grip, that are comparable to those of synthetic specialty rubbers.¹⁰ ENR with 50 mol % epoxidation (ENR50) has been shown to be polar, with properties similar to those of NBR.¹¹ ENR became a popular research subject because of its outstanding loadability with numerous fillers and reinforcement.^{12–14}

EXPERIMENTAL

Materials

ENR50 was purchased from Kumpulan Guthrie Sdn. Bhd. (Seremban, Malaysia). HD-PURs of different decomposition degrees were supplied by the Institute of Composite Materials, Ltd. (Kaiserslautern, Germany). HD-PUR 1 and HD-PUR 2 were decomposed in the presence of 10 wt % water at 230 and 180°C, respectively, in a laboratory twin-screw extruder (Haake, Karlsruhe, Germany) with poly(ester urethane)-type shoe sole production waste. The residence time during decomposition was about 4 min, and this was determined by the pigment tracer method. The melt viscosity of HD-PUR was determined with a plate/plate rheometer.⁹ The HD-PUR melt viscosity at 170°C and acetone insolubility were about 900 Pa s and 14% and about 7600 Pa s and 39% for types 1 and 2, respectively. This HD-PUR selection served in investigating whether or not the cure and mechanical characteristics were imparted by the decomposition degree of HD-PUR. The preparation of HD-PUR is described in detail in other articles.^{8,9} Other materials such as sulfur, 2,2-dithiobisbenzothiazole, zinc oxide, carbon black (grades N330 and N375), and stearic acid were supplied by Bayer (M) Sdn. Bhd. (Penang, Malaysia). The physical properties of the two grades of carbon black are given in Table I.¹⁵ All materials were used as supplied.

Formulation

The formulations shown in Table II were employed for an evaluation of the effects of different grades of HD-PUR and carbon black in ENR50 vulcanizates cured with various types of vulcanization systems.

Sample Preparation

Mixing was carried out on a laboratory-scale two-roll mixing mill (160 mm × 320 mm; model XK-160, Tokyo, Japan) in accordance with ASTM

Table I Physical Properties of Carbon Black N330 and N375 (15)

	Mean Particle Size (nm)	Surface Area (m ² /g)	DBPA (cm ³ /100 g)	Bulk Density (g/cm ³)
N330	26–36	81	104	0.365
N375	30–35	98	116	0.365

Table II Formulation for ENR50 Cures with Different Types of Vulcanization Systems

Recipe	Vulcanization System	
	CV System (phr)	Semi-EV System (phr)
ENR50	100.0	100.0
Zinc oxide	4.0	4.0
Stearic acid	2.0	2.0
Sulfur	1.8	1.5
CBS ^a	1.0	1.5
IPPD ^b	2.0	2.0
Carbon black ^c	50.0	50.0
HD-PUR ^d	Variable	Variable
Processing oil	5.0	5.0

^a *N*-Cyclohexyl-2-benzothiazole-2-sulfenamide.

^b *N*-Isopropyl-*N*-phenylenediamine.

^c Two different grades of carbon black type high abrasion furnace (HAF), that is, N330 and N375.

^d Two different grades of PUR rubber degraded hygrothermally (HD-PUR 1 and HD-PUR 2).

Standard D 3184-80. The cure times at 150°C (indicated by t_{90}) were determined with a Monsanto model MDR2000 rheometer (Swindon, England). The torque, elastic modulus, and so forth were also determined with this test. The Mooney scorch time, cure index, and Mooney viscosity (ML; 1 + 4) were determined at 150°C on a Mooney MV2000 viscometer (Swindon, England). The rubber compounds were compression-molded at 150°C into sheets 2 mm thick on the basis of their respective t_{90} values with a KAO Tieh compression-molding machine (Taipei, Taiwan) at a pressure of 10 MPa. The temperature used in this study (150°C) was earlier found to be suitable for obtaining optimum properties for ENR50 vulcanizates.¹⁶

Testing

Tensile tests were carried out according to ASTM Standard D 412 on a Monsanto T10 tensometer. Dumbbell specimens were cut from molded sheets with a Wallace die cutter (S/6/1/4) (Croydon, England). A crosshead speed of 500 mm/min was used, and the tests were performed at $25 \pm 2^\circ\text{C}$. Five specimens were tested, and the median value was used in each case.

Tear tests were carried out according to ISO Standard 34 type III with crescent shaped specimens on the aforementioned Monsanto tensometer at a crosshead speed of 500 mm/min. Five specimens were used, and the average value was calculated.

A Wallace dead-load hardness tester was used for measuring the hardness [in international rub-

ber hardness degree (IRHD)]. The related procedure followed the recommendations of ISO Standard 48 (1979).

The compression set was determined according to ASTM Standard D 395B. Specimens in the form of circular discs 13 mm in diameter and 6.3 mm thick were tested. The specimens were compressed to a 25% strain between two smooth platens at 25°C and then held there at 70°C for 24 h in an air oven.

Resilience testing was carried out on a Dunlop pendulum (Croydon, England) according to BS 903 A8. The energy not recovered in the resilience testing was the hysteresis given by $100 - \text{resilience}$.

A thermooxidative aging (TOA) study was performed according to BS 7646. The samples were placed in an air oven at 80°C for 168 h. The retention of properties was calculated as follows:

Retention (%) =

$$(\text{Value after Aging}/\text{Value before Aging}) \times 100$$

RESULTS AND DISCUSSION

Effect of the PUR Loading

Table III shows the effect of increasing the PUR concentration on the scorch time, torque maximum, torque minimum, and Mooney viscosity. The addition of both HD-PUR 1 and HD-PUR 2 does not produce any appreciable effect on the curing characteristics of ENR50 vulcanizates. This is in contrast to the results of our earlier

Table III Effect of HD-PUR Loading on Cure Characteristics of ENR50

Cure Characteristic	HD-PUR 1					HD-PUR 2			
	0	5	10	15	20	5	10	15	20
t_{90} (min)	5.0	4.3	4.7	4.9	4.9	4.6	4.9	5.0	4.6
Scorch time (min)	1.6	1.4	1.5	1.5	1.2	1.5	1.3	1.6	1.5
Maximum torque (dNm)	12.4	14.1	12.2	12.2	11.1	11.5	15.2	10.7	10.6
Mooney viscosity (MU)	7.5	6.4	12.8	7.2	7.7	7.5	11.0	6.4	8.2

investigation of NR vulcanizates.⁸ Then, t_{90} was reduced from 10.42 to 7.05 min with the incorporation of 20 phr HD-PUR 1. This was attributed to the presence of primary amine in HD-PUR that facilitated the curing of the NR vulcanizates. A similar trend was also recently reported for SBR vulcanizates.¹⁷ The absence of such reactivity for ENR50 may be attributed to the different nature of the rubber itself. Unlike both NR and SBR, ENR50 is a polar rubber. Therefore, the role of amine in HD-PUR in facilitating the curing process can be expected to be rather limited. However, a possible mechanism for explaining this phenomena is still obscure at present.

It can also be seen from Table III that, with the exception of 10 phr HD-PUR 1 and HD-PUR 2, the addition of HD-PUR generally has no notable effect on the maximum torque and viscosity of ENR50 compounds. This implies that the HD-PUR/ENR50 system can be compounded and processed in a manner similar to that used for the control ENR50 recipe. This is in agreement with the trend observed for NBR vulcanizates.⁸ This is believed to be related to the polar nature of both ENR50 and NBR. It was proven by Baker et al.¹⁸ that the epoxidation of NR results in a class of elastomers that possess chemical and physical properties similar to those of synthetic rubbers such as NBR instead of NR. The situation is quite different for NR vulcanizates, for which the incorporation of HD-PUR has been reported to reduce the Mooney viscosity significantly.⁸ The peculiar behaviors of both ENR50/HD-PUR 1 and ENR50/HD-PUR 2 at a 10 phr HD-PUR loading will be the subject of a future investigation.

Figure 1 shows the effect of the PUR loading on the tensile strength of ENR50 vulcanizates. The addition of both HD-PUR types decreased the tensile strength. A dosage of 20 phr HD-PUR 1 reduced the tensile strength by 19.2%. A similar tendency was found for the torque maximum, suggesting that the crosslink density decreased

with increasing HD-PUR concentration. The slight reduction in tensile strength and modulus at 300% elongation (M300; Fig. 2) with increasing HD-PUR loading was accompanied by a steady increase in the elongation at break (EB) of the vulcanizates. This is shown in Figure 3. EB increased from 564% to 694 and 709% in the presence of 20 phr HD-PUR 1 and HD-PUR 2, respectively. This is not surprising because the decrease in crosslink density was not substantial, whereas the dilution effect of HD-PUR enabled improved mobility of the ENR50 molecules. HD-PUR is, therefore, expected to behave as a polymeric plasticizer for ENR50. Being polar rubbers, both HD-PUR and ENR50 are capable of forming hydrogen bonds. Therefore, a positive interaction is expected between these rubbery materials. A possible mechanism is illustrated in Figure 4. A similar interaction between ENR50 and poly(vinyl chloride) was reported by Ishiaku and Mohd Ishak¹⁹ on the basis of Fourier transform infrared and dynamic mechanical analysis data. According to Mousa and Karger-Kocsis,¹⁷ the influence of HD-PUR on the tensile properties of SBR vulcanizates is rather different. The incorporation of 10 and 20 phr HD-PUR increased the tensile strength and M300, but at the expense of EB. The improvement in the degree of crosslinking of the SBR/HD-PUR vulcanizates was claimed to be responsible for the observed trend.

The effect of the HD-PUR loading on the tear strength is depicted in Figure 5. The ENR50 compound lost some of its tear strength with the addition of both types of HD-PURs, although the overall reduction was less significant. This can be attributed again to the decreased crosslinking, as discussed earlier. The scenario is similar to that observed in NBR/HD-PUR stocks.⁸ Note that the performance of ENR50 is closely matched to that of polar synthetic elastomers, including NBR.

The incorporation of both types of HD-PURs increased the compression set of the ENR50 for-

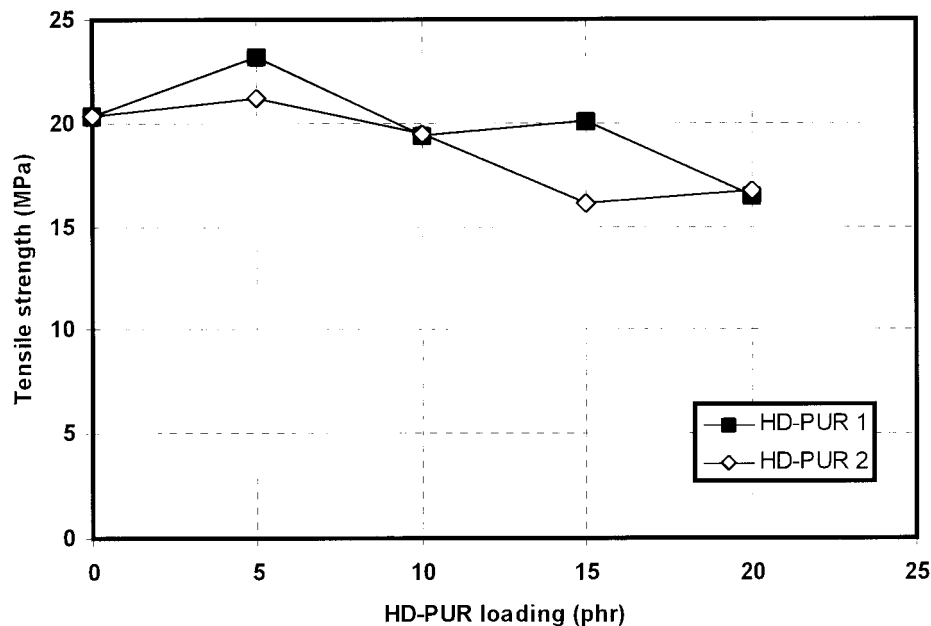


Figure 1 Effects of the types and loadings of HD-PUR on the tensile strength of ENR50 vulcanizates.

mulations (Fig. 6). The compression set increased up to 70% with the addition of 20 phr HD-PUR. This means that the elastic recovery of ENR50 was adversely affected by the presence of HD-PUR. On the basis of this and the reduction in the

values of the tensile strength, M300, and tear strength with the incorporation of HD-PUR observed earlier, it becomes obvious that under these experimental conditions, HD-PUR is not capable of providing a positive contribution to-

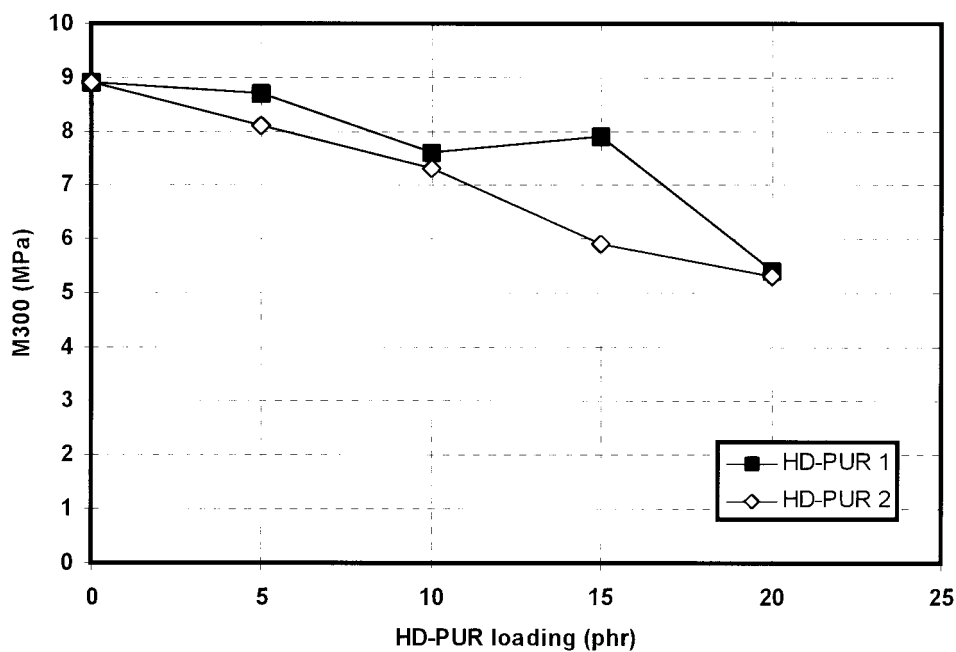


Figure 2 Effects of the types and loadings of HD-PUR on M300 of ENR50 vulcanizates.

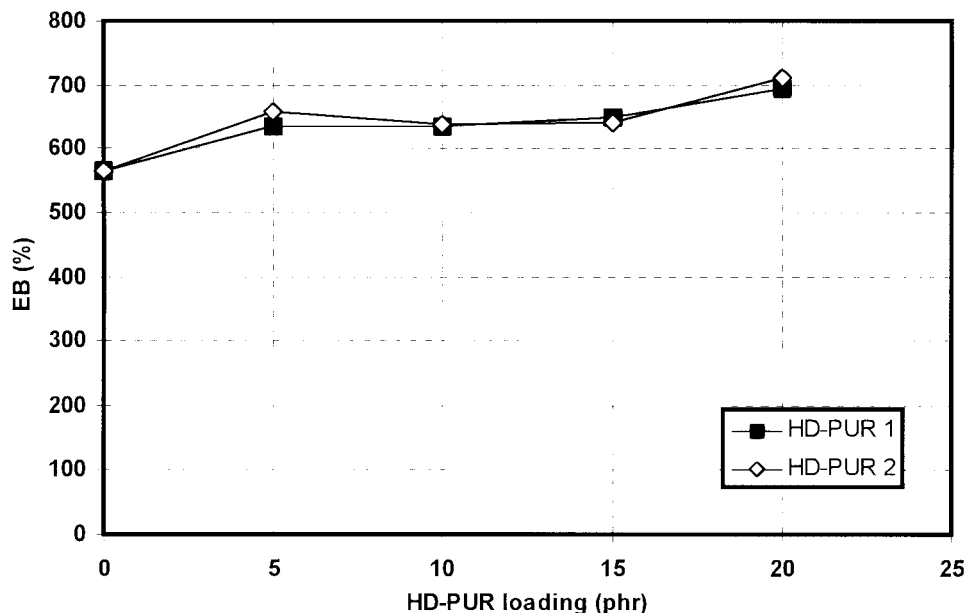


Figure 3 Effects of the types and loadings of HD-PUR on EB of ENR50 vulcanizates.

ward an enhancement of the elastic properties of ENR50 vulcanizates. On the contrary, both HD-PUR grades seem to behave as polymeric plasti-cizers.

The effect of the HD-PUR loading on the hard-ness of ENR50 vulcanizates is shown in Figure 7. Hardness decreased with increasing HD-PUR concentration. This is in tandem with the course of M300, indicating a decrease in the crosslink density with increasing HD-PUR concentration. Figure 8 shows the effect of the HD-PUR loading on the resilience of ENR50 compounds. Unlike other physical properties discussed earlier, such

as tensile and tear strengths, there was no appar-ent effect of the HD-PUR loading on the resilience of ENR50. This implies that the role of HD-PUR in ENR50 recipes is rather selective. This trend agrees well with that of the compression set (Fig. 6) which indicates that the elastic properties were reduced with increasing HD-PUR loading. A sim-ilar observation was made for HD-PUR-filled NR and NBR vulcanizates.⁸

Effect of Thermo-oxidative Aging (TOA)

Table IV shows the effect of TOA on the tensile and tear properties of HD-PUR/ENR50 vulcani-zates. The decrease in tensile strength proved slight, and so a high retention of tensile strength after TOA was confirmed. There is no particular tendency, indicating that the presence of HD-PUR plays a less significant role in the TOA pro-cess. Similar patterns can be observed with re-spect to the tear strength, although its retention is relatively lower for the formulations containing HD-PUR. EB, however, markedly decreased be-cause of TOA. This is consistent with a remark-able increase in modulus [both M100 (modulus at 100% elongation) and M300] as a result of TOA. The aging of ENR proceeds via epoxide ring-open-ing reactions that lead to the formation of ether crosslinks.¹⁹ These account for the increase in modulus and reduction in the EB percentage of ENR50 compounds.

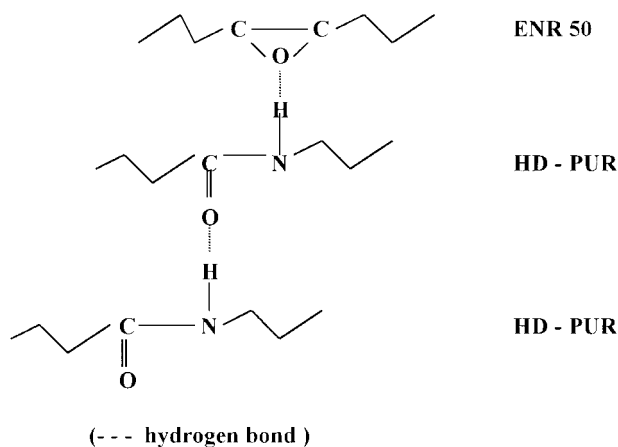


Figure 4 Schematic representation of the formation of hydrogen bonding between ENR50 and HD-PUR.

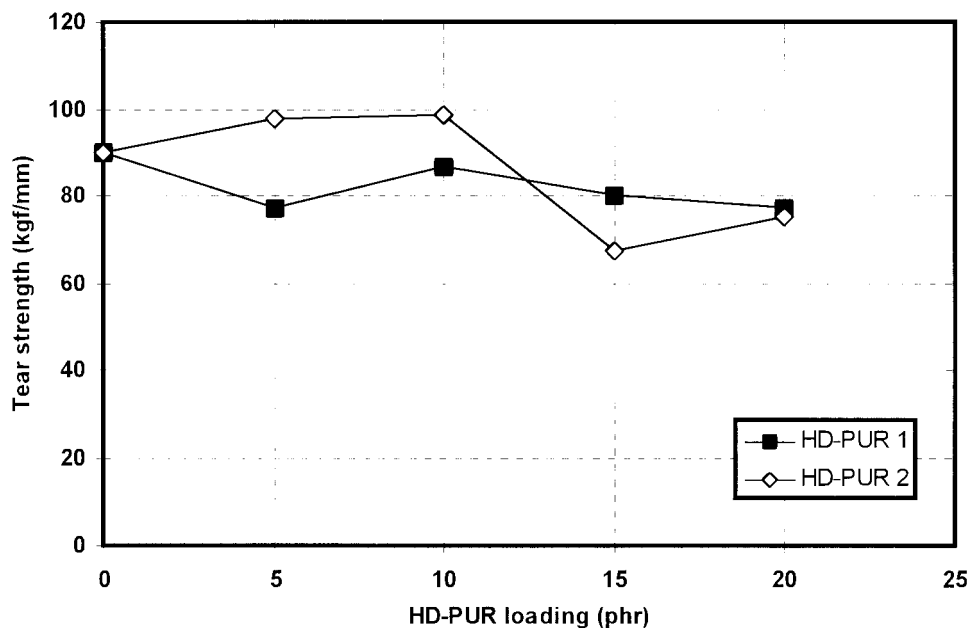


Figure 5 Effects of the types and loadings of HD-PUR on the tear strength of ENR50 vulcanizates.

Effect of the Vulcanization System

The effects of the vulcanization systems on cure characteristics and vulcanizate properties were studied for ENR50 with 20 phr HD-PUR. Table V shows the cure time t_{90} , scorch time, and torque

minimum and maximum for CV and semi-efficient vulcanization (semi-EV) systems. In general, the semi-EV system gave shorter cure times than the CV system. This shows that vulcanization is accelerated with an increasing accelerator

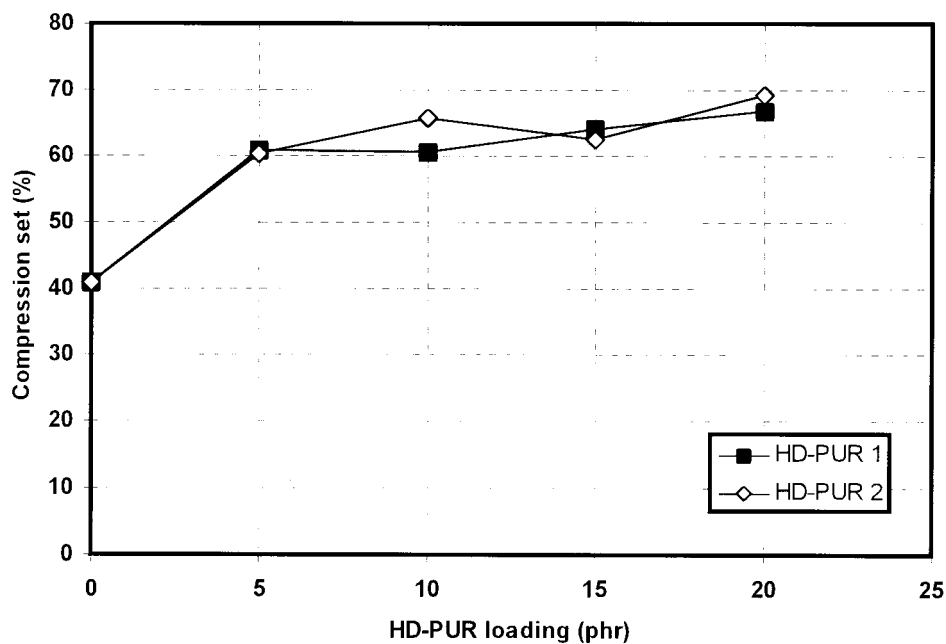


Figure 6 Effects of the types and loadings of HD-PUR on the compression set of ENR50 vulcanizates.

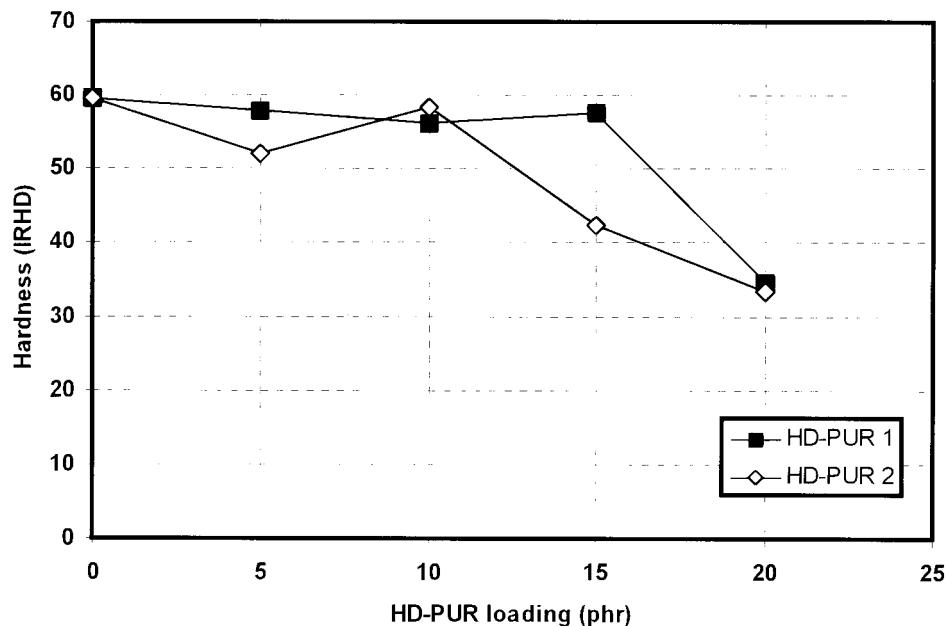


Figure 7 Effects of the types and loadings of HD-PUR on the hardness of ENR50 vulcanizates.

concentration with respect to sulfur. This feature is also reflected in the scorch time. A recent study by Sadequl et al.²⁰ on ENR (with 25 mol % epoxidation) also supported this view.

According to Bateman,²¹ the accelerator molecule interacts with sulfur to form active sulfu-

rating agents. These react with the rubber molecules by creating crosslinks. The amount of active sulfurating agents is increased with increasing accelerator concentration. Therefore, more crosslinks will be formed, and the scorch time is shortened.

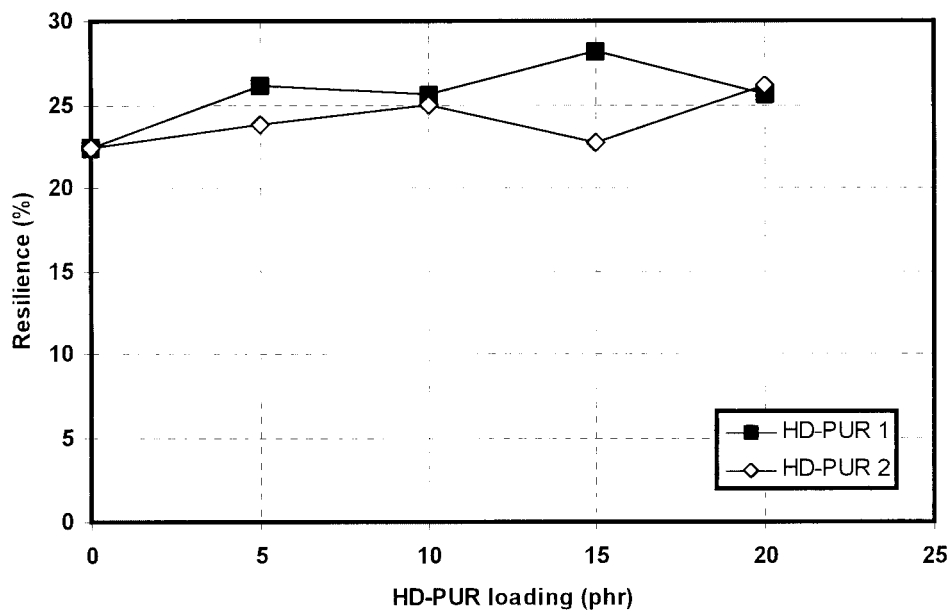


Figure 8 Effects of the types and loadings of HD-PUR on the resilience of ENR50 vulcanizates.

Table IV Effect of HD-PUR Loading on the Retention Properties of ENR50/HD-PUR Vulcanizates

Mechanical Property	HD-PUR 1					HD-PUR 2			
	0	5	10	15	20	5	10	15	20
Tensile strength (MPa)	19.2 (20.3) [94.3]	22.3 (23.2) [96.1]	17.1 (19.4) [88.2]	17.4 (20.1) [86.4]	15.0 (16.4) [97.2]	18.7 (21.2) [88.2]	16.7 (19.5) [85.7]	15.4 (16.1) [95.7]	14.4 (16.7) [86.6]
EB (%)	508 (564) [90.1]	505 (634) [79.7]	402 (633) [63.5]	432 (649) [66.6]	460 (694) [66.3]	405 (656) [61.7]	411 (636) [64.6]	421 (639) [65.9]	449 (709) [63.3]
M100 (MPa)	2.7 (2.4) [112.6]	3.7 (2.5) [151.8]	3.7 (2.4) [151.9]	3.7 (2.4) [153.2]	3.3 (1.8) [182.7]	3.9 (2.5) [159.3]	3.5 (2.4) [149.6]	3.2 (1.9) [170.4]	3.0 (1.8) [166.3]
M300 (MPa)	9.9 (8.9) [111.6]	13.3 (8.7) [152.4]	12.6 (7.6) [166.5]	11.9 (7.9) [150.2]	10.2 (5.4) [188.2]	13.6 (8.1) [166.9]	12.0 (7.3) [162.8]	10.5 (5.9) [177.7]	9.2 (5.3) [173.4]
Tear strength (kgf/mm)	84.3 (89.8) [93.8]	53.9 (77.0) [70.0]	46.1 (86.8) [53.1]	61.8 (80.2) [77.0]	51.5 (77.2) [66.8]	84.5 (97.9) [86.3]	51.4 (98.5) [52.3]	50.2 (67.1) [74.9]	43.4 (75.0) [57.9]

Numbers outside of parenthesis or brackets represent values after aging. Numbers in parentheses represent values after aging. Numbers in brackets represent percentage retention.

Table VI summarizes the effect of the vulcanization system on the mechanical properties of ENR/HD-PUR compounds. Both vulcanization systems were effective in producing vulcanizates with good mechanical strength, although semi-EV gave slightly higher values. According to Gelling and Porter,²² a semi-EV normally yields better mechanical performance than a CV system for ENR because of different crosslinking mechanisms. The CV system generates polysulfidic and disulfidic crosslinks, whereas the semi-EV system yields the same amount of polysulfidic and monosulfidic and disulfidic crosslinks. The effects of different network structures became apparent when ENR vulcanizates were subjected to cyclic strains in fatigue²³ and TOA tests.¹⁸ The CV system

gave a slightly higher compression set than the semi-EV system (Fig. 9). This could be due to TOA effects because the test was performed at 70°C for 24 h. CV-cured ENR vulcanizates are known to have poor aging stability.²² This accounts for the opposite trend shown by resilience (Fig. 8), which was determined at ambient temperature (25°C). Both properties measure elasticity, and a similar trend would otherwise have been expected. The hardness values are similar except for that of CV-cured ENR50 with HD-PUR 1 (Fig. 9). Even then, it falls within the same range for soft elastomers. The same reasoning given for mechanical properties can be used to account for this observation.

The effect of the vulcanization system on the TOA properties are summarized in Table VI. Ten-

Table V Effect of Vulcanization System on the Cure Characteristics of ENR50/HD-PUR

Cure Characteristic	CV		Semi-EV	
	HD-PUR 1	HD-PUR 2	HD-PUR 1	HD-PUR 2
t_{90} (min)	8.4	8.7	4.9	4.6
Scorch time (min)	2.1	1.9	1.2	1.5
Maximum torque (dNm)	12.1	11.0	11.1	10.6
Maximum torque – minimum torque (MH – ML; dNm)	11.3	10.3	10.0	10.6

Table VI Effect of Vulcanization System on the Retention Properties of ENR50/HD-PUR Vulcanizates

Mechanical Property	CV		Semi-EV	
	HD-PUR 1	HD-PUR 2	HD-PUR 1	HD-PUR 2
Tensile strength (MPa)	15.8 (15.2) [103.8]	15.2 (16.2) [93.6]	16.0 (16.4) [97.2]	14.4 (16.7) [86.6]
EB (%)	393 (591) [66.5]	514 (693) [74.2]	460 (694) [66.3]	449 (709) [63.3]
M100 (MPa)	3.8 (2.2) [174.9]	2.8 (1.8) [152.0]	3.3 (1.8) [182.7]	3.016 (1.8) [166.3]
M300 (MPa)	12.2 (7.1) [172.7]	8.3 (5.4) [154.1]	10.2 (5.4) [188.2]	9.2 (5.3) [173.4]
Tear strength (kgf/mm)	40.8 (64.1) [63.7]	52.5 (71.8) [73.2]	51.5 (77.2) [66.8]	43.4 (75.0) [57.9]

Numbers outside of parenthesis or brackets represent values after aging. Numbers in parentheses represent values after aging. Numbers in brackets represent percentage retention.

sile strength, EB, and tear strength were reduced, whereas moduli (M100 and M300) increased as a result of TOA. However, the difference between the two vulcanization systems is not very obvious. The presence of HD-PUR as a polymeric plasticizer could be responsible for this finding. The presence of plasticizers has been shown to arrest TOA in poly(vinyl chloride)/ENR50 blends with

an aging mechanism similar to that of ENR vulcanizates.¹⁹

Effect of the Carbon Black Type

Semi-EV-cured ENR50 vulcanizates containing 20 phr HD-PUR were studied with different grades of carbon black at a 50 phr loading. The

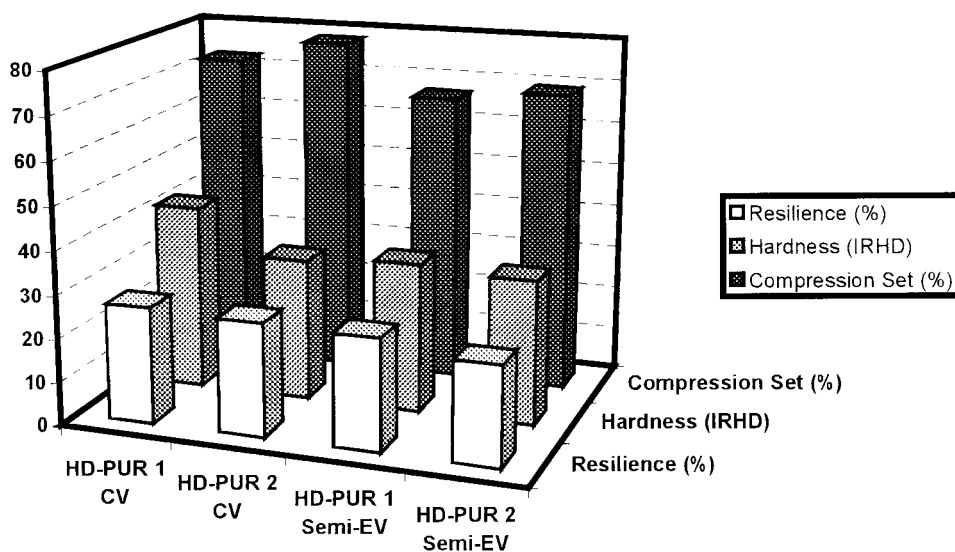


Figure 9 Effects of the types of vulcanizations on the compression set, resilience, and hardness of ENR50/HD-PUR vulcanizates.

Table VII Effect of the Type of Carbon Black on the Cure Characteristics of ENR50/HD-PUR

Cure Characteristic	N375		N330	
	HD-PUR 1	HD-PUR 2	HD-PUR 1	HD-PUR 2
t_{90} (min)	6.6	4.9	4.9	4.6
Scorch time (min)	2.3	2.0	1.2	1.5
Maximum torque (dNm)	12.1	13.1	11.1	10.6
Mooney viscosity (MU)	17.9	17.3	7.7	8.2
Maximum torque – minimum torque (dNm)	11.4	12.5	10.5	10.1

effects of the carbon grade on the curing characteristics of ENR50/HD-PUR blends are tabulated in Table VII. N375 yielded slightly higher scorch and cure times than N330. However, the Mooney viscosity for N375 is higher than that of N330. The difference in cure characteristics may be attributed to the fact that each type of filler possesses different filler properties, such as surface area, surface activity, and particle size (see Table I). The increase in the surface area of N375 increases the viscosity of the compound. The similarity of the values for scorch time and t_{90} may be due to the meager difference between the surface areas of the two fillers. The black with a higher surface area would be expected to give shorter scorch and cure times, although the difference in the surface areas of the two grades is about 17 m²/g.

Table VIII illustrates the effect of the carbon black grade on the mechanical properties of ENR50 vulcanizates. The tensile strength of the N375-filled vulcanizate is superior to that of the N330-containing recipe, as expected. Being smaller, N375 particles have a higher surface area available for interaction with the rubber molecules, which guarantees improved reinforcing properties. M300 also shows the same trend.

However, EB for the formulation with N330 is higher than that for the N375-filled vulcanizate. This observation has implications similar to those for M300, for which N330 shows lower values.

The slightly higher tear strength of N375-filled ENR50 vulcanizates shown in Table VIII corroborates the reinforcing efficiency of N375. This may again be attributed to the relatively larger surface area of N375, which allows better interaction with the rubber matrix. The change in the compression set is parallel to that of mechanical properties, for which N375 filling resulted in superior values. As expected, hardness changed similarly to the modulus. This demonstrates the effect of the filler particle size, surface area, and structure on both properties.

CONCLUSIONS

On the basis of this study on the application of HD-PUR to ENR50 formulations, the following conclusions can be drawn:

1. The incorporation of HD-PUR into ENR50 compounds resulted in slightly lower mechanical properties. As the property reten-

Table VIII Effect of the Type of Carbon Black on the Mechanical Properties of ENR50/HD-PUR

Mechanical Property	N375		N330	
	HD-PUR 1	HD-PUR 2	HD-PUR 1	HD-PUR 2
Tensile strength (MPa)	18.3	19.2	16.0	16.4
EB (%)	625	639	694	709
M300 (MPa)	6.3	6.1	5.6	5.0
Tear strength (kgf/mm)	91.6	84.8	77.2	75.0
Compression set (%)	33.1	45.6	66.7	69.2
Resilience (%)	24.9	24.0	25.6	22.7
Hardness (IRHD)	59.8	59.5	34.5	33.3

tion of the formulations with HD-PUR was quite high, one can suggest that the amine-rich HD-PUR acted as a polymeric plasticizer. The presence of HD-PUR did not influence the vulcanizate properties when various vulcanization systems (i.e., CV and semi-EV) were used. Moreover, HD-PUR improved the resistance to TOA of ENR vulcanizates cured by a conventional vulcanization system. This effect is similar to that of low molecular weight plasticizers in ENR50 blends.

2. HD-PUR/ENR50 vulcanizates with carbon black grade N375 showed mechanical properties superior to those of N330-filled counterparts. It was also proven that the presence of HD-PUR in ENR50 recipes did not adversely affect or alter the function of fillers.

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