Effect of Type of Accelerators and Curing Temperature on Vulcanisate Properties of NR/ENR50 Blends.

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Introduction

Blending of rubbers is extensively used in the industry to achieve desirable combination of properties at a reasonable cost. In rubber blends it is imperative that both the component rubbers are vulcanized almost to the same extent and are also vulcanized to one another across the interface to obtain acceptable physical properties. Due to the higher solubility of sulphur in unsaturated rubbers and the greater affinity of many accelerators for more polar rubbers, significant difference in the cross-link density of the phases of rubber blends can result. In addition, if the rate of vulcanization varies considerably between the elastomers, depletion of the curatives in the faster curing component can cause curative migration and further cure imbalance. When the component rubbers are technologically compatible and having comparable cure rates it is not too difficult to achieve acceptable vulcanisate properties as in the case of blends like NR/PB or SBR/PB which are widely used in tyre treads. It is much more difficult to achieve useful blends of NR with specialty rubbers like nitrile rubber, epoxidised natural rubber (ENR), EPDM, butyl rubber etc. due to high level of incompatibility, large differences in curative migration or cure rate between elastomer. Recent studies have shown the importance of identifying cure systems which will give near even cross-link distribution in elastomer blends containing rubbers differing in polarity (1).

ENR50 is a chemically modified form of NR (having 50 mole % epoxidation) having oil resistance comparable to that of NBR and air impermeability close to that of butyl rubber (2). Recently it has been reported that blending of 20-50 parts of ENR50 with NR could reduce the air permeability of NR from half to one fourth of its original value (3). These blends were vulcanized using a peroxide system. Due to the widely differing polarity of these rubbers, commercial utilization of this finding recquires proper selection of sulphur based cure system to achieve desirable vulcanisate properties. The present study reports the influence of the type of accelerators on the cure characteristics and gum vulcanisate properties of the NR/ENR50 blends. The effect of cure temperature (140 – 170^{0}C) on vulcanisate properties of these blends was also studied.

Experimental

The rubbers used in this study were NR (ISNR5) and epoxidised natural rubber with 50 mole % epoxidation (ENR50), both produced at the pilot plant facility at the Rubber Research Institute of India. Other ingredients were standard commercial grade chemicals.

NR and ENR 50 masterbatches were prepared according to the formulation given in Table 1 using a laboratory type Banbury internal mixture at 40^{0}C, 70 rpm for 5 minutes. Cross blending of the masterbatches were also carried out using similar conditions for 2 minutes. Curatives were added in a two-roll mill. Tables 2-4 give the curative formulations used. A semi-EV cure system with sulphur: accelerator ratio 1.5:1.5 was used. CBS was arbitrarily selected as the base accelerator and same molar concentration of other accelerators were used. In a similar manner, the level of secondary accelerator was selected as 0.1 phr TMTM and same molar level was used for all other secondary accelerators.

Cure characteristics were determined using a Monsanto Rheometer R100 and the test samples were cured to its optimum cure time (t_{95} min). Vulcanisate properties of the blends were determined as per ASTM standards. For compounds prepared using selected cure systems, the estimation of cure time and vulcanization of the test samples were carried out at 140, 150, 160 and 170°C.

Results and Discussion

Cure characteristics and vulcanisate properties

The cure characteristics NR and ENR50 gum compounds and its 50:50 blends are given in Table 5. The cure rate is substantially high for ENR (CRI= 44.4) than for NR (CRI= 26.7). Though the mechanism of vulcanization in these rubbers are essentially similar, ENR cures faster as the isolated double bonds react more rapidly than continuous double bonds (4). CBS and MBS based compounds show comparable cure time .The maximum torque attained in these systems were also comparable showing that the number of cross links formed are comparable. DCBS based compounds cured at a much slower rate except DCBS/TMTM system The maximum torque attained were also much less when compared to the other two systems.

Tensile properties

Table 6 shows the vulcanisate properties of NR and ENR 50 cured using CBS and its blends cured using different accelerator systems. Both NR and ENR show high gum strength due to their ability to strain crystallize. Among CBS system, those blend vulcanizates cured using CBS plus secondary accelerators showed high tensile strength, 24.8-27.1 MPa. Modulus and elongation at break are high and comparable. From these results it can be assumed that CBS based accelerator system could generate fairly even distribution of cross-links in both NR and ENR phases.

Among the MBS series, MBS alone and MBS/TMTM system showed lower tensile values while MBS/DPG and MBS/ MBTS systems imparted high tensile strength. Modulus values were also lower when MBS alone was used while other systems showed comparable modulus values. All vulcanizates prepared using DCBS based accelerators showed lower tensile properties because of the lower level of total cross links formed. This is evident from the lower modulus values as well as from the lower maximum rheometric values.

Tear strength

Except in DCBS systems tear strength values are higher than that of the individual NR and ENR50 gum vulcanizates. Such synergism in tear stregth is reported earlier also in heterogeneous rubber blends (5). Such improvement in tear strength properties of the blend is attributed to a better intercross linking between phases. Thus the blend vulcanizates prepared using cure systems CBS/TMTM, CBS/DPG and MBS /MBTS which showed higher tensile strength and high tear strength indicates that its two phases cross linked evenly and might have sufficient inter cross linking at the interphase.

Other vulcanisate properties

Table 7 give blend vulcanizate properties other than tensile and tear strength. Shore A hardness of the blend vulcanizates prepared using CBS and MBS based cure systems are comparable while that of DCBS based cure system was lower. ENR showed considerably higher compression set when compared with NR vulcanizate. In blends, the compression set varied depending on the type of accelerators used; lowest for CBS/TMTM system and highest for DCBS systems. Heat build up values are comparable for CBS and MBS based systems and had values in between NR and ENR 50 gum vulcanizates

Effect of cure temperature

From the forgoing discussion it can be seen that the best tensile, tear strength properties and lower compression set values were obtained using CBS/TMTM, CBS/DPG and MBS/MBTS systems. In order to study the effect of cure temperature on vulcanisate properties of NR/ENR 50 blends, these blends were cured at 140,160 and 170 C also.

Fig.1 shows variations of tensile strength with cure temperature. Tensile strength was comparable when cured at 140^{0}C-160^{0}C. Modulus at 300% elongation also showed similar trend. Fig. 2 shows the effect of cure temperature on tear strength which indicates that in all three systems the highest value was obtained for vulcanisates cured at 150^{0}C and then decreased when the cure temperature is increased. Compression set values were generally lower for samples cured at 140 and 150 ^{0}C compared to that cured at 160 and 170 ^{0}C (Fig.3). These results show that, though the best results were obtained at 150 C, the effect of cure temperature on vulcanisate properties were marginal for the three cure systems studied except at 170^{0}C. This in turn indicates that the diffusion and partitioning of curatives between NR and ENR 50 was not significantly influenced by cure temperature.

Conclusion

The effect of type of accelerators on cure characteristics and vulcanisate properties of 50:50 blend of NR/ENR50 was studied. Three different sulphenamide accelerators; CBS, MBS and DCBS were used as primary accelerators at equimolar concentrations along with TMTM, DPG and MBTS as secondary accelerators. CBS/TMTM, CBS/DPG and MBS/MBTS systems showed better tensile and tear strength properties compared to that of NR and ENR 50 gum vulcanisates. Other physical properties were in between that of NR and ENR 50 vulcanisates. Vulcanisate properties of the blend using these systems cured at 140 to 160^{0}C were comparable and that cured at 170^{0}C showed reduction in properties indicating that curative migration was not significantly influenced by temperature. DCBS series showed poor properties compared to two other systems.

References

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Table1 : Formulation for NR and ENR master batches

Ingredients	Amount, phr	
NR	100	-
ENR50	--	100
Calcium stearate	-	5
ZnO	5	5
Stearic acid	2	2
Antioxidant HSL	2	2

Table 2 : CBS cure system

Curatives	Amount, phr			
S	1.5	1.5	1.5	1.5
CBS	1.5	1.5	1.5	1.5
TMTM	-	0.1	-	-
DPG	-	-	0.11	-
MBTS	-	-	-	0.17

Table 3 : MBS cure system

Curatives	Amount, phr			
S	1.5	1.5	1.5	1.5
MBS	1.43	1.43	1.43	1.43
TMTM	-	0.1	-	-
DPG	-	-	0.11	-
MBTS	-	-	-	0.17

Table 4 : DCBS cure system

Curatives	Amount, phr			
S	1.5	1.5	1.5	1.5
DCBS	1.97	1.97	1.97	1.97
TMTM	-	0.1	-	-
DPG	-	-	0.11	-
MBTS	-	-	-	0.17

Table 5 : Cure characteristics of the blends

Compound	Minimum Torque, dN.m	Maximum torque, dN.m	Cure time, t_{95}, min	Cure rate Index
NR	7.0	59.75	12.8	26.7
ENR 50	3.0	41.0	6.5	44.4
CBS	3	43.0	9.0	40.0
CBS/TMTM	3.5	44.0	7.5	50.0
CBS/DPG	4.0	45.0	7.5	44.4
CBS/MBTS	3.0	43.0	9.0	40.0
MBS	2.0	43.0	9.75	25.0
MBS/TMTM	2.5	45.0	6.75	33.3
MBS/DPG	2.0	44.0	9.25	26.6
MBS/MBTS	3.0	46.0	9.0	26.7
DCBS	3.0	27.0	27.0	5.0
DCBS/TMTM	3.0	27.0	8.2	21.5
DCBS/DPG	4.0	33.0	27.0	4.2
DCBS/MBTS	2.5	35.0	16.5	8.3

Table 6 : Tensile and tear strength of NR/ENR50 blends (50:50)

Sample	Tensile strength, MPa	M100, MPa	M200, MPa	M300, MPa	EB, %	Tear strength, N/mm
NR (CBS)	22.1	0.98	1.52	2.23	616	33.0
ENR50 (CBS)	20.0	0.96	1.52	2.1	620	26.0
CBS	22.0	0.94	1.42	2.08	647	45.5
CBS/TMTM	27.1	1.01	1.58	2.4	653	45.3
CBS/DPG	26.0	0.94	1.45	2.15	680	51.1
CBS/MBTS	24.8	0.97	1.49	2.19	669	44.2
MBS	15.7	0.873	1.34	1.97	615	33.5
MBS/TMTM	16.0	0.98	1.54	2.21	605	42.8
MBS/DPG	24.1	0.94	1.45	2.14	675	40.8
MBS/MBTS	27.9	0.99	1.53	2.3	688	44.3
DCBS	6.54	0.663	0.93	1.29	611	14.0
DCBS/TMTM	12.2	0.78	1.13	1.61	636	26.6
DCBS/DPG	12.4	0.77	1.13	1.61	638	18.2
DCBS/MBTS	16.8	0.75	1.13	1.63	666	22.7

Table 7 : Vulcanisate properties of NR/ENR50 blends

Sample	Hardness Shore A	Compression set, 70^0C/ 22h	Heat build up, ^oC	Resilience, %
NR (CBS)	34	19.9	4	76.0
ENR50 (CBS)	35	41.7	13	31.9
CBS	29	44.6	9	51.2
CBS/TMTM	30	26.9	9	51.2
CBS/DPG	30	36.1	9	45.7
CBS/MBTS	29	33.6	9	50.0
MBS	32	31.4	12	50.6
MBS/TMTM	31.5	34.0	10	44.0
MBS/DPG	31.5	36.2	9	55.0
MBS/MBTS	32	33.2	9	45.2
DCBS	24	55.4	14	49.4
DCBS/TMTM	28	54.6	14	50.8
DCBS/DPG	26	56.4	15	44.6
DCBS/MBTS	28	44.0	11	48.8

Fig1.Variations of tensile stregth of NR/ENR50 blends with temperature

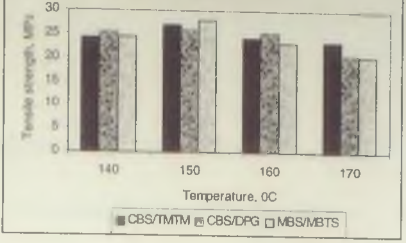

Fig.2 Variations of tear strength of NR/ENR50 blends with cure temperature

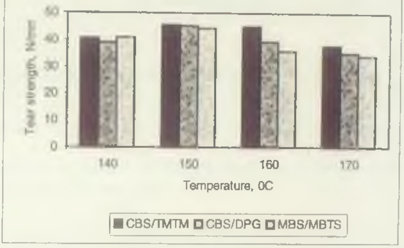

Fig3: Effect of cure temperature on compression set of NR/ENR50 blends