PEROXIDE VULCANIZATION OF EPOXIDISED NATURAL RUBBER

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ABSTRACT

Sulphur cured Epoxidised natural rubber (ENR) shows poor ageing properties due to the sulphur acid catalysed ring opening reactions of epoxy groups. Peroxide curing of ENR is expected to give superior ageing properties. The present paper reports the mechanical as well as thermal ageing properties of ENR 50 cured using dicumyl peroxide (DCP). Gum and carbon black filled systems of ENR were studied and compared with that of natural rubber (NR) vulcanizate. Both NR and ENR vulcanizates showed comparable properties except for compression set and resilience. ENR vulcanizates showed superior retention in tensile properties compared to NR vulcanizate when aged at 70 and 100°C. Significant reduction in compression set could be achieved by the addition of a co-agent.

INTRODUCTION

Crosslinking of Epoxidised natural rubber (ENR) with sulphur yields vulcanizates with poor ageing properties due to sulphur acid catalysed ring opening reactions of the epoxy groups with the formation of ether crosslinks [1]. The acids are produced by thermal decomposition of oxidised sulfides. In order to obtain good ageing properties peroxide curing system have been proposed. Peroxide crosslinking is known to impart good ageing resistance and excellent resistance to compression set. However, it requires longer cure cycles and the vulcanizates have lower tensile strength and elongation, lower tear strength and abrasion resistance than sulphur cured vulcanizates [2]. In order to overcome these disadvantages, co-agents at varying concentrations are used with peroxide vulcanizing agents to increase the crosslinking efficiency, scorch safety and to improve physical properties of vulcanizates [3]. Acrylic co-agents are one of the crosslinking monomer that is widely used to improve physical properties and the processability of peroxide cured elastomers [4].

The objective of the present study is to investigate the effect of peroxide cure system on the mechanical as well as thermal properties of ENR 50 (ENR with 50 mol % epoxidation). Gum and HAF filled compounds of NR and ENR 50 were prepared with DCP as the curing agent. To study the effect of co-agent on degree of crosslinking and improvement in properties, zinc dimethacrylate was incorporated into the ENR compound.

EXPERIMENTAL

Materials

The natural rubber used for the study was technically specified form of rubber (TSR) obtained from the Pilot Crumb Rubber Factory of Rubber Board, Kottayam –9. The TSR used was ISNR-5 grade having the Mooney viscosity 70.

ENR 50 obtained from the ENR pilot plant at RRII having 50-mole % epoxidation and having the Mooney viscosity 118.

Co-agent – SR 634 (zinc dimethacrylate) supplied by Sartomer Company, USA. Other chemicals used were of commercial grade.

Preparation of compounds

Gum and HAF filled compounds of NR and ENR 50 were prepared as per the formulation given in Table 1.

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Table 1. Formulation of mixes

Ingredient	A_1	A_2	A_3	A_4
Natural rubber (ISNR 5)	100	-	100	-
Epoxidised natural rubber (ENR 50)	-	100	-	100
Calcium stearate	-	3	-	3
HAF black	-	-	50	50
Paraffinic oil	-	-	5	5
Dicumyl peroxide (DCP)	4	4	4	4

Cure characteristics of the compounds were determined using rheo TECH MD+ at 160°C to their respective optimum cure time. Properties of the vulcanizates were determined as per the relevant ASTM standards. Ageing of the vulcanizates was carried out at 100°C for 3 days and at 70°C for 7 days.

To study the effect of co-agent on the vulcanizate property of peroxide cured ENR, 5 phr of co-agent SR 634 was incorporated into the carbon black filled ENR compound (A_5). Cure characteristics, technological properties and ageing characteristics were studied. Volume fraction (Vr) of rubber was determined by the equilibrium swelling method in toluene at 30°C according to Ellis and Welding [5]. Swelling studies in ASTM oils were carried out as per ASTM D 471-98 at 28 and 70°C for 24 h.

RESULTS AND DISCUSSION

a. Cure characteristics

Cure characteristics of gum and filled vulcanizates are given in Table 2.

Table 2. Cure characteristics of compounds

Parameter	A_1	A_2	A_3	A_4
Minimum torque, dN.m	3.5	1.9	4.5	3.6
Maximum torque, dN.m	11.1	9.1	18.7	13.3
Δ, Rheometric torque, dN.m (Max – Min)	7.6	7.2	14.2	9.7
Optimum cure time, t_{90} at 160°C, min	19.0	21.0	21.0	23.0
Mooney viscosity, ML (1+4) at 100°C	37.2	36.0	76.3	75.2

It was observed that for both gum and filled mixes, the minimum and maximum torque were lower for the ENR mix. A slight increase in the optimum cure time was observed for the ENR mix. Mooney viscosity was comparable for both compounds.

b. Mechanical properties

Mechanical properties of gum and filled vulcanizates are given in Table 3.

Table 3. Technological properties of vulcanizates

Parameter	A_1	A_2	A_3	A_4
100% Modulus, Mpa	0.77	0.73	3.27	3.19
200% Modulus, Mpa	1.45	1.16	12.45	10.02
300% Modulus, Mpa	2.43	1.72	22.56	-
Tensile strength, Mpa	4.15	4.28	24.02	18.56
Elongation at break, %	435	455	309	283
Tear strength, N/mm	19.00	14.20	39.40	38.64
Compression set, %				
70°C, 22h	7.53	14.73	6.30	18.70
100°C, 22h	14.73	27.69	14.20	28.40
Hardness, Shore A	27	27	55	52
Heat build-up, ΔT, °C	19	23	26	43
Resilience, %	76.09	40.52	54.76	25.31

Marginal increase in modulus values was observed for NR mix. Tensile strength and elongation at break were comparable for gum mixes but for filled mixes higher values were observed for NR compounds. Tear strength was lower for ENR gum mix but comparable values were obtained for filled mixes. Compression set at 70 and 100°C were higher for both gum and filled ENR mixes. Hardness remained the same for gum mixes and were comparable for filled mixes. Low resilience and high heat build-up were obtained for both gum and filled ENR compounds.

c. Ageing resistance

The ageing resistance of the vulcanizates were measured by determining the tensile properties before and after ageing at 100°C for 3 days and at 70°C for 7 days. The results are given in Tables 4 and 5 respectively.

Table 4. Percentage retention of tensile properties after ageing at 100°C for 3 days

Parameter	A_1	A_2	A_3	A_4
100% Modulus	79	93	72	116
200% Modulus	67	91	63	110
300% Modulus	64	95	-	-
Tensile strength	59	76	60	97
Elongation at break	91	91	91	96
Tear strength	83	85	90	98

Table 5. Percentage retention of tensile properties after ageing at 70°C for 7 days

Parameter	A_1	A_2	A_3	A_4
100% Modulus	101	104	94	110
200% Modulus	102	103	88	107
300% Modulus	-	107	-	-
Tensile strength	49	83	78	95
Elongation at break	55	94	87	97
Tear strength	83	87	90	97

The retention of strength and modulus for both gum and filled ENR mixes were better over NR mixes. This may be due to lower number of double bonds in ENR. This also shows that the ageing property of ENR is critically affected by the cure system. Almost equal retention of tear strength and elongation at break were observed for gum mixes but for filled compounds ENR showed better retention than NR.

Retention of modulus at 100 and 200 percentage elongation for gum mixes aged at 70°C was comparable but for filled mixes ENR showed better retention than NR. Retention of tensile strength, tear strength and elongation at break for the ENR mixes were better over NR mixes.

A comparison of the cure characteristics and technological properties of NR, ENR and ENR cured with co-agent are given in Tables 6 and 7 respectively.

Table 6. Comparison of cure characteristics of NR, ENR and ENR cured with co-agent

Parameter	A_3	A_4	A_5
Minimum torque, dN.m	4.5	3.6	3.1
Maximum torque, dN.m	18.7	13.3	24.4
Δ, Rheometric torque, dN.m (Max – Min)	14.2	9.7	21.3
Optimum cure time, t_{90} at 160°C, min	15.0	23.0	34.5
Mooney viscosity, ML (1+4) at 100°C	76.3	75.2	63.5

*A_5 = A_4 + 5 phr Saret 634

Table 7. Comparison of technological properties of NR, ENR and ENR cured with co-agent

Parameter	A_3	A_4	A_5
100% Modulus, Mpa	3.27	3.19	5.30
200% Modulus, Mpa	12.45	10.02	12.60
300% Modulus, Mpa	22.56	-	-
Tensile strength, Mpa	24.02	18.56	18.00
Elongation at break, %	309	283	230
Tear strength, N/mm	39.40	38.64	58.30
Compression set, %			
70°C, 22h	6.30	18.70	7.71
100°C, 22h	14.20	28.40	20.62
Hardness, Shore A	55	52	74
Heat build-up, ΔT, °C	26	43	33
Resilience, %	54.76	25.31	27.15
Crosslink density, Vr	0.2236	0.1994	0.2662

With the addition of co-agent to the ENR filled system, maximum and rheometric torque increased and the values are higher than that for NR mix (Table 6). Optimum cure time increased while Mooney viscosity lowered for the ENR mix containing the co-agent.

From Table 7 it was observed that the modulus values were improved with the addition of co-agent. This is also supported by the Vr values. Tensile strength remained the same while EB decreased. Substantial increase in tear strength and hardness was there for the ENR mix containing the co-agent and the values were much higher than that for NR mix. With the addition of co-agent, marked reduction in compression set was noticed for the ENR mix and the set value obtained at 70°C was comparable to that for NR mix. But at 100°C, the NR mix got the lowest set value. This may be due to the less effectiveness of the co-agent at higher temperature . Reduction in heat build-up was also noticed when the co-agent was included in the ENR mix. Resilience was not significantly affected by the addition of co-agent.

Comparison of the ageing resistance at 100 and 70°C are given in Tables 8 and 9 respectively.

Table 8. Percentage retention of tensile properties after ageing at 100°C for 3 days

Parameter	A_3	A_4	A_5
100% Modulus	72	116	128
200% Modulus	63	110	-
Tensile strength	60	97	95
Elongation at break	91	96	80
Tear strength	90	98	96

Table 9. Percentage retention of tensile properties after ageing at 70°C for 7 days

Parameter	A_3	A_4	A_5
100% Modulus	94	110	111
200% Modulus	88	107	119
Tensile strength	78	95	98
Elongation at break	87	97	103
Tear strength	90	97	99

At both the temperatures almost equal retention of strength and modulus were observed for ENR and ENR cured with co-agent.

Comparison of oil swelling behaviour of NR, ENR and ENR cured with co-agent in ASTM No. 2 and 3 oils both at 28°C and 70°C for 24 h are represented in Table 10.

Table 10. Comparison of oil swelling behaviour of NR, ENR and ENR cured with co-agent

Change in Mass (%)	A_3	A_4	A_5
28°C, 24 h			
ASTM No.2 oil	16.400	0.930	0.994
ASTM No.3 oil	52.408	3.383	1.851
70°C, 24 h			
ASTM No.2 oil	61.175	3.783	4.598
ASTM No.3 oil	135.430	15.749	16.579

It can be seen that both ENR and ENR crosslinked with co-agent showed excellent resistance to oil swelling compared to NR.

CONCLUSIONS

Both NR and ENR gum vulcanizates showed comparable properties except for compression set, heat build-up and resilience. In HAF filled system, modulus, tensile strength and EB were lower whereas compression set is higher for ENR compound. Reduced hardness and resilience and increased heat build-up were obtained for the ENR compound. The addition of co-agent substantially increased the tear strength and hardness of ENR vulcanizate. Compression set and heat build-up were also considerably reduced. ENR exhibited excellent thermal ageing and oil resistance when compared with that of NR vulcanizate.

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OP-98 Peroxide Vulcanization of Epoxidised Natural Rubber

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