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Cure Characteristics and Vulcanizate Properties of NBR/ENR Blends

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ABSTRACT

Effect of substituting small amounts of ENR 50 (0-30 parts) in NBR compounds on cure characteristics and vulcanizates properties in both gum and carbon black/ silica filled systems were investigated. A silane modified NBR/silica system was also studied for comparison. Cure characteristics and vulcanizate properties of both gum and filled systems were improved with the incorporation of 15 parts of ENR 50. Substantial reduction in cure time was observed for both the systems studied. Tensile strength, modulus and tear strength improved, while oil resistance of the blend remained unchanged. Mechanical properties of NBR/ENR/Silica vulcanizates were comparable to that of silane modified NBR/silica system, indicating that ENR acts as a reinforcement modifier. Ageing properties of NBR are not adversely affected by the incorporation of 15 parts of ENR 50.

Key words: Nitrile rubber, Epoxidised natural rubber, Ageing/Oil resistance, Reinforcement modifier

INTRODUCTION

Blending of rubbers is important in view of the improved properties that can be achieved by blend composition, choice of additives, blending techniques and vulcanizing conditions. Three fundamental aspects of such blending are to create the desired phase morphology through mixing and processing steps, to get uniform crosslink density by control of migration of the compounding ingredients and to improve adhesion between the phases through crosslinks formed across the interphase[1]. Blending of rubbers having close solubility parameters and comparable cure rates leads to technologically compatible blends with acceptable physical properties. Compatibility in these systems can further be improved by co-crosslinking the blend constituents, if reactive sites are available[2,3].

Epoxidised natural rubber (ENR), a modified form of natural rubber, has a unique set of properties offering high strength due to its ability to undergo strain crystallization, along with increased oil resistance and reduced gas permeation. Nitrile rubber (NBR) exhibits excellent resistance to oils and greases, high abrasion resistance, low compression set and good ageing resistance but has relatively poor strength properties. A combination of the oil resistance properties of this rubber and the strength properties of natural rubber would be an ideal compromise, but the difference in polarity and molecular structure between the two rubbers results in such blends having unsatisfactory properties. Recent studies by *George et al.*,[4] indicated that when ENR is blended with NBR using a carefully selected cure system and blending process, vulcanizates with excellent mechanical properties and oil resistance are obtained. These studies also indicated that ENR can form self vulcanizable blends with NBR.

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The objective of the present study is to investigate the effect of substituting small proportions of NBR with ENR 50 (0-30 parts) on cure characteristics, and vulcanizate properties in both gum, carbon black and silica filled NBR compounds. A silane modified NBR/silica system was also studied for comparison.

EXPERIMENTAL

Materials

Nitrile rubber, Aparene N 423-NS supplied by Apar Industries Ltd. (India) (acrylonitrile content-33 %), epoxidised natural rubber with 50 mole % epoxidisation (ENR 50) prepared at the pilot plant facility at the Rubber Research Institute of India, Kottayam, hydrated silica (Ultrasil VN_3) and coupling agent Si-69 [bis (3-triethoxypropyl)-silyl tetra sulphide] (Degussa AG, Germany) were used as received. The other ingredients were of commercial grade.

Preparation of compounds

The formulations and conditions used for the preparation of NBR/ENR 50 gum blends are given in Table1. Cure characteristics of the compounds were determined using Monsanto Rheometer R-100 at 150° C. Test samples were moulded at 150° 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 70 ^{0}C for 7 days and at 100 ^{0}C for 48h. 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 ^{0}C for 24 h.

Carbon black and silica filled blends were prepared as per the formulations given in Table 5 in a laboratory model internal mixer (Shaw Intermix KO) at a mix temperature of 40° C and at 60 rpm for 10 min. The bound rubber content in the blends (R_B) was determined by the method described by Wolff *et al.*, [6].

RESULTS AND DISCUSSION

Unfilled blends.

(a) Cure characteristics

Cure characteristics of the gum vulcanizates are given in Table 2. The results show that minimum torque and maximum torque increased with the addition of ENR The optimum cure time and scorch time systematically decreased and the cure rate index increased as the proportion of ENR was increased in the blends. Mooney viscosity values also increased significantly with increased ENR content. An increase in the minimum rheometric torque, an indication of compound viscosity, and increased Mooney viscosity may be attributed to NBR-ENR interaction through the acrylonitrile and epoxy group respectively (*George et al.,*[4]).

(b) Mechanical properties

Stress-strain properties of the samples are represented in Figure 1. The stress-strain properties were significantly modified with the incorporation of ENR.

Mechanical properties of the blends are given in Table 3. Modulus at 100, 200 and 300% elongation increased significantly with the addition of 5 parts of ENR. Marginal increase was observed with further increase in ENR up to 15 parts, beyond which it decreased with the increase in ENR content. Same trend was observed for tensile strength and tear strength, while elongation at break (EB) showed a continuous decrease with increase in ENR content. Rebound resilience increased with the addition of 5 parts of ENR and remained constant with further increase in ENR content. Hardness also showed same trend. A reduction in heat build-up was observed with increased ENR concentration. Compression set showed an increasing trend with increase in ENR content. Increase in modulus, tensile strength, tear strength and reduced heat build up may be attributed to increased crosslinking resulting by the reaction between CN group and the epoxy group in NBR and ENR respectively. This is also supported by Vr studies (Table 4). It is known that the epoxy group react with CN group in an alkyl nitrile compound.[7].

(c) Oil swelling

Vr increased with the addition of 5 parts of ENR 50 and then decreased when the ENR content was further increased. Crosslinks might have resulted not only from the sulphur cross-links, but also from the NBR-ENR interaction. A comparison of oil swelling of these blends with that of NBR gum vulcanizate in ASTM oils did not show any appreciable difference (Table 4). This indicates that substitution of NBR with ENR 50 up to 30 parts did not influence the oil resistance of NBR.

(d) Ageing resistance

Figures 2 and 3 show the ageing resistance in terms of retention of tensile strength and modulus of NBR/ENR 50 blends after ageing at 70° C for 7 days and at 100° C for 48 h respectively. Retention of tensile strength and modulus for the ENR substituted samples were better over the unmodified sample. Almost equal retention in properties was observed at both the temperatures. Retention in tensile strength was maximum for mixes with 10-15 parts of ENR.

Carbon black and silica filled blends

(a) Cure characteristics and bound rubber

The above results are summarized in Figure 4. It can be seen that the mechanical properties increased with the increase in ENR content, reached a maximum at 15 parts of ENR in the blend and then decreased with further increase in ENR content. Therefore further studies by filled systems were carried out using 85/15 blend composition.

Cure characteristics and bound rubber measurements of the carbon black as well as silica filled blends are presented in Table 6. Properties of an NBR/silica system modified by a silane coupling agent (Si 69) were also determined for comparison. Cure characteristics of carbon black and silica filled compounds were modified when NBR was substituted with

ENR50. The minimum rheometric torque, an indication of compound viscosity, was higher for the ENR incorporated blends. Maximum torque and differential torque were also higher for NBR/ENR blends in both carbon black and silica filled blends compared with those of the respective NBR compounds. A substantial reduction in optimum cure time (30 to 14.5 min) was observed when NBR was reinforced with carbon black. This was further reduced to 10.5 min when 15 parts of NBR were substituted with ENR. Similar trend was observed for scorch time also. However, addition of silica to NBR increased cure time to 49.5 min and this was significantly reduced in NBR/ENR 50 blends (27.5 min) Reduction in cure time in NBR/ENR/silica system was higher than even the silane modified NBR/silica system (34 min).

Bound rubber (R_B) measurement is conventionally being done to assess the level of rubber-filler interaction: the higher the bound rubber, the higher the rubber–filler interaction [8]. Silica – filled mixes containing ENR 50 and silane coupling agent and the NBR-ISAF and NBR- ENR – ISAF mixes showed higher R_B values than those of the unmodified sample. ENR modified samples gave much higher R_B values than the samples modified with coupling agent and NBR-ISAF mix. The unusually high values might have resulted from the combined effect of polymer-filler interaction and the gel content resulting from the NBR-ENR interaction mentioned earlier. Tan et al [8] reported that the gel resulting from the polymer-polymer interaction could contribute to higher values of bound rubber. The higher R_B values in NBR-ISAF mix over that of the NBR-silica mix is attributed to the larger polymer filler interaction for carbon blacks in NBR.

(b) Mechanical properties

A comparison of the stress-strain properties of the filled systems are presented in Figure 5. The stress-strain properties were modified with the incorporation of ENR 50 for both carbon black and silica filled blends.

Table 7 represents the mechanical properties of carbon black and silica filled blends. A slight increase in 100% modulus was observed for carbon black and silica-filled mixes containing ENR 50 over the respective unmodified mixes. Modulus at 300 % elongation was higher for NBR/ENR/carbon black system than the NBR/carbon black system. For NBR/ENR/silica vulcanizate, a substantial increase in modulus was observed over NBR/silica vulcanizates (4.4 to 13.6 MPa). For the silica filled NBR/ENR blend, the modulus value obtained was marginally higher than that obtained for NBR/silica containing Si-69. This indicates that ENR substantially increases the dispersibility of silica in NBR..

Improved tensile strength and reduced elongation at break (EB) are considered to be the criteria for higher filler reinforcement [9]. Increased tensile strength and reduced EB were observed for ISAF and silica-filled mixes containing ENR 50. Marked increase in vulcanizate properties were observed for silica filled vulcanizate containing 15 parts of ENR 50. NBR/ENR 50/silica vulcanizates gave tensile strength comparable with those of Si-69 modified NBR/silica and NBR-ISAF vulcanizates.

Improvement in tear strength and abrasion resistance are also indicative of enhanced filler reinforcement [10]. Increase in tear strength was observed for silica-filled mixes containing ENR 50 or Si 69 over the unmodified mix and the values obtained for composites modified with coupling agent and ISAF could also be achieved for NBR-silica composite modified with ENR. Substitution of NBR with ENR or incorporation of a coupling agent in NBR-silica composite improved abrasion resistance to a greater extent than that of the unmodified mix.

Improved tear strength and abrasion resistance observed for the ENR modified composites can be attributed to the enhanced polymer-polymer and polymer-filler interactions achieved through ENR. NBR-ENR blend with ISAF gave almost the same tear strength and abrasion resistance as that obtained for NBR-ISAF composite. NBR-silica composites modified with ENR showed a lower resilience value compared to that modified with Si-69. The resilience values observed for the carbon black filled mixes were closer to that of the silica filled one modified with ENR.

An increase in hardness was observed for carbon black and silica filled mixes containing modifiers over the unmodified mixes and the increase is more pronounced for NBR-ENR blends. This may due to the increased crosslink density resulting from NBR-ENR interaction. For silica filled composites, a reduction in compression set with incorporation of ENR was observed. The set values obtained for NBR-silica composites modified with ENR was closer to that obtained for the coupling agent and ISAF filled vulcanizates.

(c) Oil swelling

Oil swelling values of the filled blends are presented in Table 8. Incorporation of ENR did not influence the oil resistance of NBR in both carbon black as well as silica filled systems.

(d) Ageing resistance

Figures 6 to 8 show the ageing resistance in terms of retention of tensile strength, elongation at break and tear strength of carbon black and silica filled blends after ageing at 100° C for 24, 48 and 72 h. It can be seen from the figures that for both carbon black and silica filled systems, the retention of the properties after ageing were comparable with those of the control samples. This shows that incorporation of ENR up to 15 parts did not adversely affect the ageing resistance of NBR.

CONCLUSIONS

Blending of small quantities of ENR 50 with NBR improved the cure characteristics and physical properties of both gum and filled vulcanizates. Blending of 15 parts of ENR with NBR substantially reduces the cure time in gum as well as in silica filled compounds. A marginal reduction in cure time was observed for carbon black filled system. Tensile strength, tear strength, hardness and abrasion resistance were significantly higher for NBR/ENR gum vulcanizate compared to those of NBR gum vulcanizate. The properties of NBR/ENR/silica vulcanizate were comparable to those of silane modified NBR/silica system indicating that ENR acts as an interface modifier. Oil resistance and ageing properties of NBR were not affected by the incorporation of up to 15 parts of ENR 50.

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Table 1. Formulation of gum compounds

Ingredient	A	B	C	D	E	F
NBR	100	95	90	85	80	70
ENR 50	-	5	10	15	20	30
Zinc oxide	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0
CBS *	1.0	1.0	1.0	1.0	1.0	1.0
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5

* N - cyclohexyl-2-benzthiazyl sulphenamide

Table 2. Cure characteristics of gum compounds

Parameter	A	B	C	D	E	F
Minimum torque, dN.m	5.0	10.0	10.5	12.0	13.0	13.0
Maximum torque, dN.m	60.0	67.5	68.0	67.0	67.0	63.0
Δ Rheometric torque, dN.m (Max. -Min)	55.0	57.5	57.5	55.0	54.0	50.0
Optimum cure time (t_{95}) at 150°C, min	30.0	18.0	16.0	14.0	12.5	12.5
Scorch time (ts_2) at 150°C, min	14.0	9.0	8.0	6.5	6.5	7.5
Cure rate index, $100/(t_{95}-ts_2)$	6.25	11.1	12.5	13.3	16.7	17.8
Mooney viscosity, ML (1+4) 100°C	35.0	80.7	98.4	100.1	99.7	125.0

Table 3. Mechanical properties of gum vulcanizates

Parameter	A	B	C	D	E	F
Modulus at 100% elongation, MPa	*0.94*	*1.95*	2.07	*2.19*	*1.79*	*1.80*
Modulus at 200% elongation, MPa	1.24	3.57	4.44	4.52	3.84	3.43
Modulus at 300% elongation, MPa	1.52	4.40	5.19	5.30	4.95	4.75
Tensile strength, MPa	2.37	8.53	11.69	12.40	11.60	10.01
Elongation at break, %	498	376	351	363	342	332
Tear strength, N/mm	21.34	33.32	34.52	35.14	32.89	29.40
Resilience, %	45.93	58.37	58.37	60.38	59.71	59.02
Hardness, Shore A	36	45	46	46	45	42
Abrasion loss, mm^3	59.33	57.96	61.07	72.16	93.09	99.10
Compression set, %	39.31	47.50	50.00	52.03	52.33	52.65
Heat build-up, ΔT, °C	25	22	20	21	19	20

Table 4. Vr and oil swelling of gum vulcanizates

Parameter	A	B	C	D	E	F
Vr	.2511	.2806	.2745	.2724	.2670	.2554
Oil swelling Change in mass, %						
ASTM No. 1 oil	2.80	1.92	1.89	1.64	1.55	1.11
ASTM No.2 oil	1.61	2.69	2.69	2.28	2.00	1.63
ASTM No. 3 oil	3.82	3.17	3.15	4.0	4.39	3.59

Table 5. Formulation of filled systems

Ingredient	Ac	Dc	As	Ass	Ds
NBR	100	85	100	100	85
ENR 50	-	15	-	-	15
Zinc oxide	4	4	4	4	4
Stearic acid	1	1	1	1	1
ISAF	50	50	-	-	-
Ultrasil VN3	-	-	50	50	50
DOP	5	5	5	5	5
CBS	1	1	1	1	1
DPG*	-	-	1.5	1.5	1.5
Sulphur	1.5	1.5	1.5	1.5	1.5
Si-69	-	-	-	4	-

* Diphenyl guanidine

Table 6 Cure characteristics and bound rubber content

Parameter	Ac	Dc	As	Ass	Ds
Minimum torque, dN.m	10	23	21	14	26
Maximum torque, dN.m	70	92	98	114	105
Δ Rheometric torque, dN.m (Max. –Min.)	60	69	77	100	79
Optimum cure time (t_{90}) at 150°C, min.	14.5	10.5	49.5	34.0	27.5
Scorch time (ts_2) at 150°C, min.	4.5	2.5	8.0	4.5	5.0
Cure rate index, $100/(t_{95}-ts_2)$	10.0	12.5	2.3	3.4	4.5
Bound rubber (R_B)	34.81	45.76	27.16	31.36	41.59

Table 7. Mechanical properties of filled systems

Parameter	Ac	Dc	As	Ass	Ds
Modulus at 100% elongation, MPa	3.1	4.1	1.8	3.3	3.8
Modulus at 300% elongation, MPa	13.6	18.2	4.4	12.8	13.6
Tensile strength, MPa	23.4	25.8	19.5	23.9	23.7
Elongation at break, %	458	445	677	446	456
Tear strength, N/mm	64.7	65.3	55.9	64.7	66.0
Abrasion loss, mm^3	77.2	78.6	106.3	78.5	84.0
Resilience, %	37.7	36.7	43.4	43.9	42.8
Hardness, Shore A	64	70	70	72	74
Compression set, %	32.5	32.3	41.2	31.0	34.0
Heat build-up, ΔT, °C	65	62	71	61	59

Table 8. Oil swelling of filled systems

Change in mass (%)	Ac	Dc	As	Ass	Ds
28 ^{0}C, 24 h					
ASTM No. 1 oil	1.8187	1.5472	0.9889	0.7152	0.7253
ASTM No. 2 oil	1.5314	0.7873	1.5132	1.0304	1.0183
ASTM No. 3 oil	2.2047	1.1780	1.0742	0.7816	0.9930
70 ^{0}C, 24 h					
ASTM No. 1 oil	-0.5187	-0.6932	-0.1392	-0.0402	0.0249
ASTM No. 2 oil	0.7522	0.7750	1.0154	0.9107	0.8080
ASTM No. 3 oil	3.8362	3.5896	2.4340	2.8279	2.6233

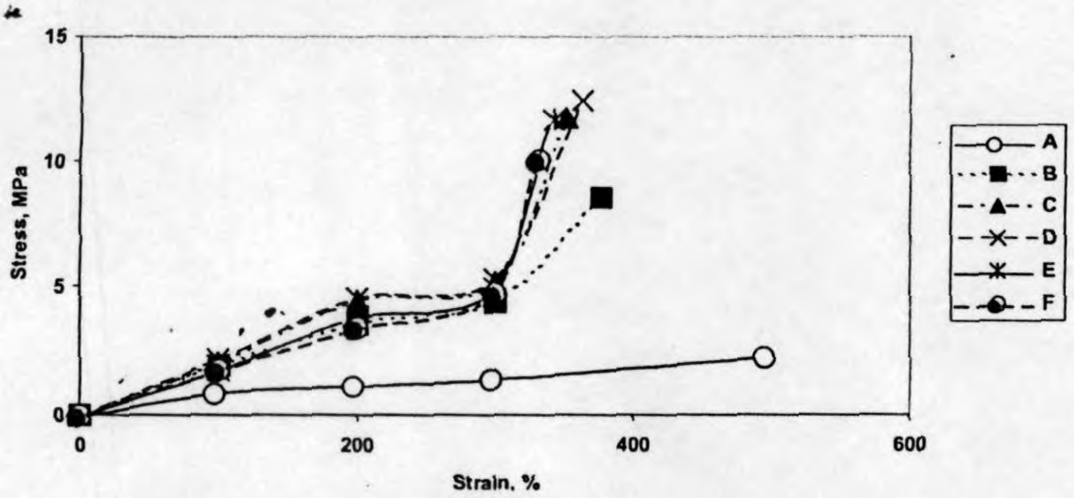

Fig. 1 Comparison of the stress-strain property of NBR-ENR

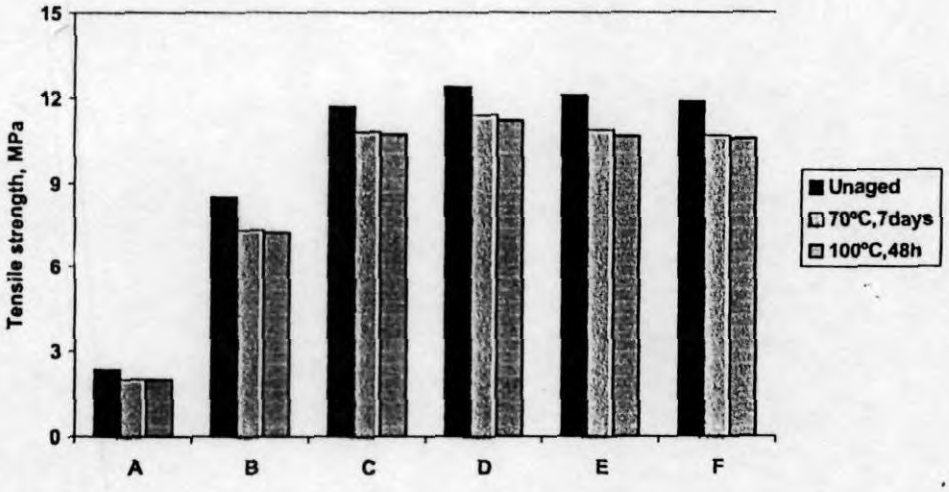

Fig. 2 Ageing resistance of NBR-ENR gum vulcanizates

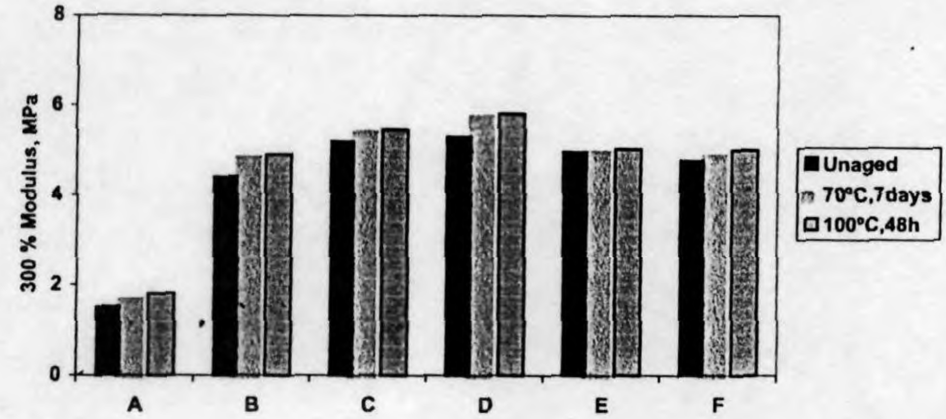

Fig. 3 Ageing resistance of NBR-ENR gum vulcanizates

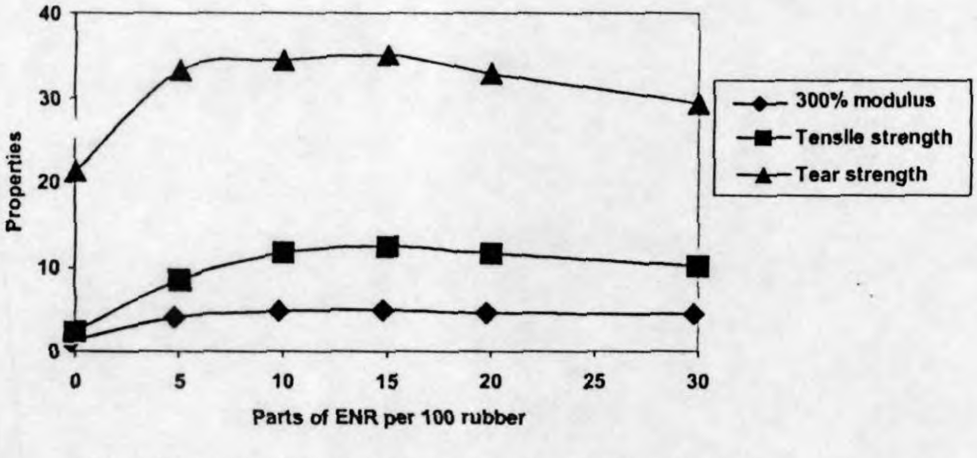

Fig. 4 Gum vulcanizate property vs. ENR content

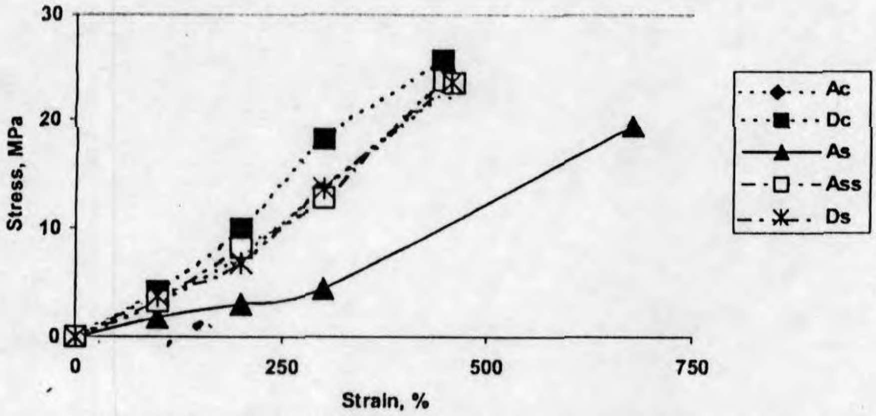

Fig. 5 Comparison of the stress-strain property of filled NBR-ENR systems

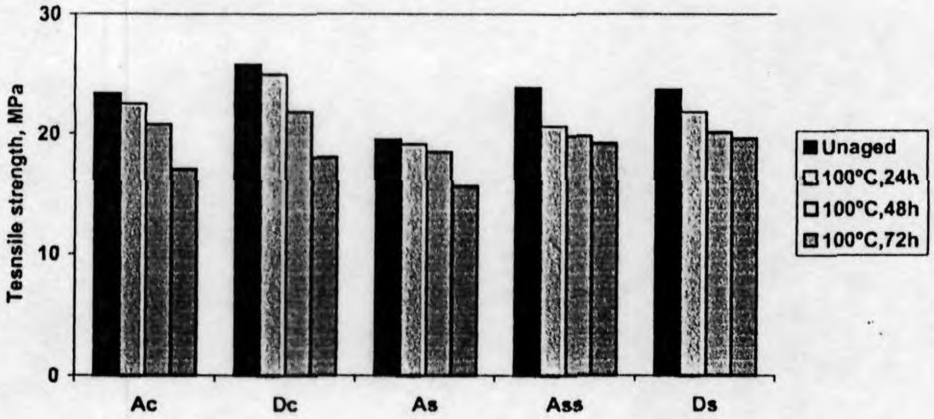

Fig. 6 Ageing resistance of NBR-ENR filled vulcanizates

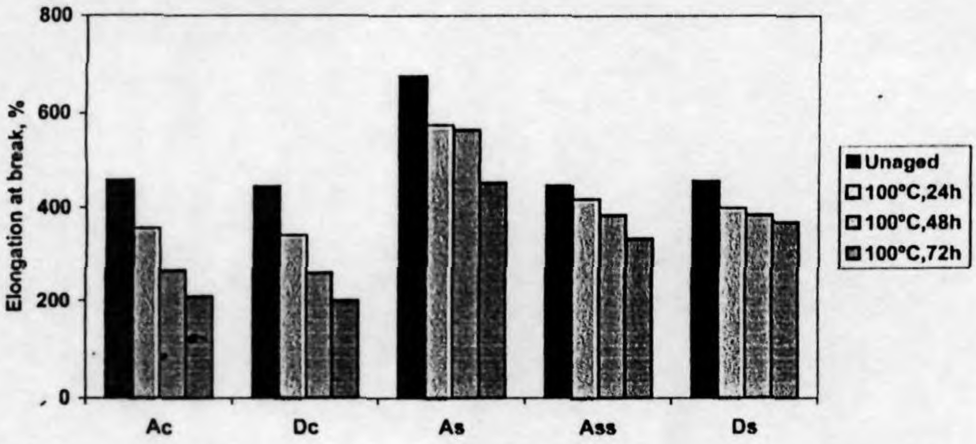

Fig. 7 Ageing resistance of NBR-ENR filled vulcanizates

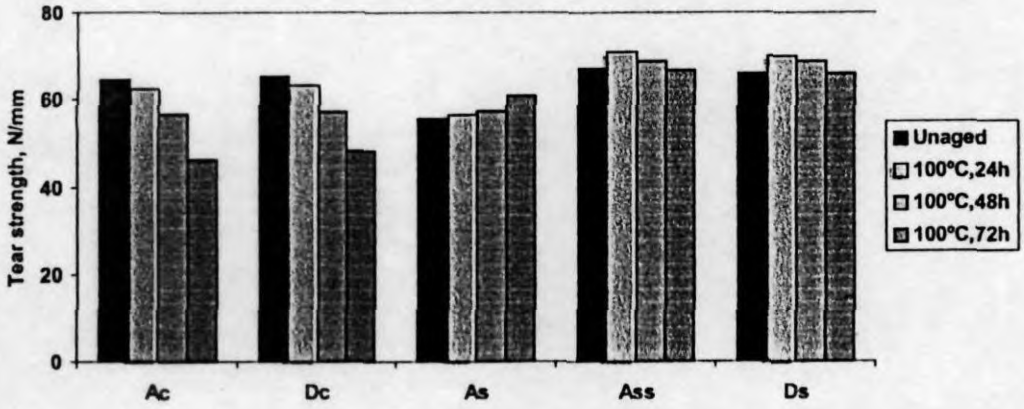

Fig. 8 Ageing resistance of NBR-ENR filled vulcanizates