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DEGRADATION BEHAVIOUR OF BLENDS OF NATURAL RUBBER WITH SPECIALITY RUBBERS: EFFECT OF HEAT, OIL, OZONE AND RADIATION

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Degradation behaviour of natural rubber (NR) and its 50/50 blends with four synthetic rubbers *viz.*, hydrogenated nitrile rubber (HNBR), ethylene propylene diene rubber (EPDM), chloroprene rubber (CR) and acrylonitrile butadiene rubber (NBR) were evaluated with respect to heat, oil, ozone and radiation as NR degrades very easily under these conditions. All the blends exhibited better ageing resistance than pure NR. Among the blends, NR/HNBR showed remarkable degradation resistance under all the conditions. Though NR/EPDM exhibited better heat and ozone resistance, its oil ageing resistance was very poor and had only very low initial tensile properties. NR/NBR showed excellent oil, ageing and radiation resistance, but its heat and ozone resistance were very poor. NR/CR showed lower degradation resistance than pure NR.

Key words: Blends, Degradation resistance, Natural rubber, Synthetic rubber.

INTRODUCTION

There is an ever increasing technical interest in the use of dissimilar rubber blends in order to improve specific vulcanizate properties, such as tensile properties and degradation resistance. Blending of polymers is an important and widely accepted method to produce commercially useful materials. Blending can combine the characteristic properties of the polymers to get new materials with tailored properties rapidly and economically. Unfortunately, blends of immiscible elastomers are often accompanied with the reduction in properties like modulus and tensile strength. For blends of elastomers of low olefinic content, the poor strength properties are a consequence of cure rate incompatibility between the polymers (Loadman *et al.*, 1989). Natural rubber (NR) though having excellent dynamic mechanical properties, is highly prone to degradation by heat and weathering due to its unsaturated structure. Blends of NR with specialty elastomers have been used in many commercial applications (Kozlowski, 1995; Bhat *et al.*, 2003; Baker *et al.*, 1986). NR blends with ethylene propylene diene rubber have been used for better weather resistance and with acrylonitrile butadiene rubber for oil/fuel resistance (Suma *et al.*, 1993; Karnika *et al.*, 1998). Blending of butadiene rubber (BR) with NR (Freitas de Castro *et al.*, 2003)

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improved the processing characteristics and abrasion resistance.

In real service life, rubber products are exposed to ageing, which is a combination of factors such as dynamic flexing, heat, oxygen, ozone, ultra violet light, high-energy radiations and various liquids. For long-term performance, sustaining the desired properties is as important as obtaining them initially. Hence, it is essential to study the ageing characteristics of the vulcanizates to assess the serviceability of products.

In this paper, 50/50 blends of NR with four speciality elastomers *viz.*, HNBR, EPDM, CR and NBR were prepared and evaluated for mechanical properties and ageing resistance on exposure to heat, oil, ozone and radiation.

MATERIALS AND METHODS

NR used for this study was Indian Standard Natural Rubber (ISNR 5), obtained from the Pilot Crumb Rubber Factory, Rubber Board, Kottayam, India. HNBR used was Zetpol 2010 of Nippon Zeon, Japan with 36% bound acrylonitrile content. The iodine value was 11 g/100g and Mooney viscosity ML (1+4) 100 °C, 85. NBR used was butadiene acrylonitrile copolymer of medium acrylonitrile content, Chemaprene N3309 supplied by Synthetics and Chemicals Ltd., Barely, U.P., India. EPDM used was Royalene 521, manufactured by Uniroyal Chemical Co., U.S.A., of medium molecular weight distribution with E/P ratio 52/48, ENB 5%, and Mooney viscosity ML (1+4)100°C, 50. Neoprene (W type) was obtained from Du Pont de Nemours Co., Germany. It consists of chloro 2 butylene in trans 1, 4 addition (85%), cis 1, 4 addition (10%), 1, 2 addition (1.5%) and 3, 4 addition (1%). All other chemicals used were of rubber grade.

ASTM oil Nos.1, 2 and 3 used were manufactured by R. E Carroll, Inc., Trenton New Jersey and supplied by Apar Ltd., Mumbai, India.

The mixes were prepared on a laboratory size two-roll mixing mill (325 x 150 mm) at a friction ratio of 1:1.25 according to ASTM D 3182-89 by careful control of temperature and time of mixing. Master batches were prepared as per Table 1 and then cross-blended for 50/50 compositions. Different elastomers differ in their cure characteristics. For NR/NBR sulphur cure was given for both the phases. Curatives used for NR/EPDM and NR/HNBR blends were different for both phases, due to the relative difference in affinity for curatives. For NR/CR, CBS/S /metal oxide cure was selected as CR is curable by metal oxides. Cure time was recorded at 160^{0}C using a Monsanto rheometer R100 according to ASTM D 2084-01. The samples were

Table 1. **Formulation of mixes**

Ingredient	NR	NBR	CR	EPDM	HNBR
Rubber	100	100	100	100	100
Zinc oxide	5	5	5	-	-
Stearic acid	1	2	-	-	-
Sulphur	1.5	1.3	-	-	-
CBS[a]	1.5	0.16	-	-	-
MBT[b]	-	0.16	-	-	-
Magnesium oxide	-	-	4	-	-
NA 22[c]	-	-	0.5	-	-
DCP[d]	-	-	-	6	6

a- N-cyclohexyl-2-benzothyazyl sulphenamide

b- Mercaptobenzothiazole

c- N-isopropyl N'phenyl p-phenylene diamine

d- Dicumylperoxide

vulcanized to their respective optimum cure time in a hydraulic press at 160°C at a pressure of 45 kg /cm^2.

The tensile properties and tear resistance of the vulcanized blends were measured on a Zwick universal testing machine (model 1474) at a cross head speed of 500 mm/ min. according to ASTM D 412:98 and ASTM D 624:98 respectively. The hardness of the cured compounds was measured according to ASTM D 2240:97 using Shore A durometer. Compression set of the compounds was measured according to ASTM D 395:02 by test method B. Resilience of the samples was measured using a Dunlop tripsometer (ASTM D 2632:96).

Ageing studies

Thermal ageing of the samples was carried out in an air circulating oven at 150 ± 2°C for 24 hours according to ASTM D 573:99. Ozone ageing was conducted at a temperature of 38.5°C and at an ozone concentration of 50 pphm (generated by an UV quartz lamp) in an ozone chamber, of MAST Development Co, U.S.A. as per ASTM D 1149-81. B type specimens were tested in duplicate in the form of bent loops. Rectangular strip of 95 x 25 x 2 mm cut in the grain direction from tensile sheets were folded and tied at 25mm length from the edges to get the required strain (>20%). These were then conditioned for 24 h and exposed to ozonized air in the chamber. Surfaces of the samples were scanned on an image analyzer of LEICA Q 500 IW and recorded as photo prints.

Oil resistance of the blends was determined according to ASTM D 471:98. Test specimens of circular shape (diameter 20mm and thickness 2 ± 0.1 mm) were punched and weighed accurately. The test specimens were then immersed in ASTM oil No. 1, 2 and 3 in a squat dish for 5 days at 28, 70 and 100°C. At the end of the immersion period, the specimens were removed, cooled to room temperature by transferring them to a cool clean portion of the test liquid for 30 minutes. Then the specimens were removed and quickly dipped in acetone at room temperature, blotted with a filter paper and weighed accurately. The percentage change in mass was calculated as

$$\Delta M = \frac{(M_2 - M_1)}{M_1} \times 100$$

Where M_1 - initial mass of the specimen
M_2 - mass of the specimen after immersion.

For studying the change in tensile properties, dump bell shaped test samples were immersed in ASTM no.2 oil at room temperature for 5 days and the properties were recorded.

Radiation resistance was studied by irradiating dumbbell shaped tensile test samples of 2 ±0.2 mm thicknesses with gamma (ϒ) rays in a Gamma chamber 5000. The samples were irradiated for different durations at a radiation dose of 0.3 M rad / h in air at room temperature. The tensile properties were measured before and after irradiation.

RESULTS AND DISCUSSION

Cure characteristics

For NR sulphur cure (semi efficient vulcanization) was selected, as it results in good mechanical properties. The possibility of interfacial cross-links in blends, during sulphur cure has been demonstrated by Tinker (1990). It is expected that during covulcaniztion, due to the more homogeneously distributed crosslinks, comparatively higher strength properties can be obtained. Figure 1 shows the rheographs of NR and its blends at 160 °C. It was observed that blend of NR with HNBR registered the highest torque and that with CR, the lowest. Cure characteristics are given in Table 2. Scorch time of the blends were lower than pure NR. Optimum cure time was higher for the blends with EPDM and HNBR, probably due to the peroxide cure.

Table 2. **Cure characteristics of NR and its blends at 160 °C**

Mix	CRI	M_H, dNm	M_L, dNm	t_{90}, min.	ts_2, min.
NR	99.92	11.34	0.96	6.24	5.24
NR/NBR	58.45	14.31	0.97	5.23	3.52
NR/CR	24.32	7.13	0.79	8.54	4.43
NR/EPDM	8.83	13.12	1.47	13.21	1.89
NR/HNBR	7.96	16.99	1.22	14.50	1.94

Table 3. **Mechanical properties of NR and its blends**

Property	NR	NR/NBR	NR/CR	NR/EPDM	NR/HNBR
Tensile strength, MPa	21.4	17.6	12.5	4.8	17.9
Elongation at break, %	620	870	895	330	320
Modulus 100%, MPa	1.44	0.95	0.91	1.58	1.25
Modulus 300%, MPa	3.24	1.75	1.52	3.85	2.53
Tear strength, kg/cm	30.6	25.1	17.2	22.5	20.5
Hardness, Shore A	42	42	36	46	44
Compression set, %					
at 125 °C/ 22 h	56.6	59.3	78.8	23.7	42.6
at 150 °C/ 22 h	87.4	68.14	96.5	32.8	56.1

Mechanical properties

Mechanical properties of NR and the blends are given in Table 3. All the blends exhibited lower tensile and tear strength than NR indicating lower level of cross-linking due to the thermodynamic incompatibility of these elastomers with NR as a result of the difference in their solubility parameter or saturation level. Blends of NR with NBR and HNBR gave comparably higher tensile strength than other two blends, which is in accordance with the higher rheometric torque due to the higher level of crosslinking. NR/EPDM blend showed very low tensile properties, probably due to the incompatibility resulting from the large difference in their saturation level (Brown *et al.*, 1990) and also due to the lower gum tensile strength of EPDM (Allen, 1992). Even though NR and CR are having similarity in their molecular structure, the difference in polarity and cure mismatch leads to lower level of crosslinks (Fig. 1) and hence lower mechanical properties. NR/CR blend showed lowest modulus, tear strength and highest elongation at break and compression set values. Better values of hardness and compression set

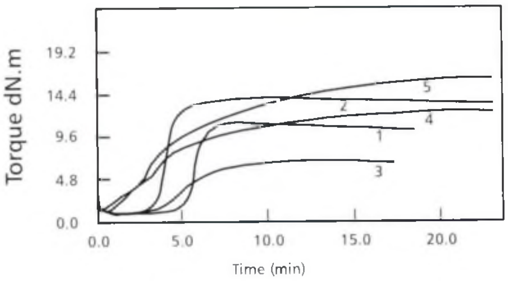


Fig. 1. Rheographs of NR (1) and 50/50 blends with NBR (2), CR (3), EPDM (4) and HNBR (5).

are shown by the blends with NBR and HNBR. NR/EPDM blend showed very low compression set at elevated temperature due to the comparatively higher heat resistance of EPDM.

Ageing characteristics

Rubber vulcanizates are degraded by thermal, mechanical and chemical means. Mainly heat, humidity, solvents, light, ozone and radiation accelerate degradation. The extent of degradation depends on the type of polymer matrix and the nature and distribution of crosslinks employed (Barker, 1988; Abou Helal *et al.,* 2005). Very poor degradation resistance of NR towards heat and weathering is attributed to its unsaturated backbone.

Thermal ageing

High performance and long-term heat and weather resistance are key requirements for many rubber components. Figure 2 shows the retention of properties of NR and the blends after air ageing at 150°C for 24 h. NR showed very poor ageing resistance. During high temperature thermal ageing in presence of oxygen, chain scission occurs at the double bond of the elastomer leading to change in molecular characteristics. This results in the overall decrease in their physical properties due to the lower extension of the molecular chains. The drastic reduction in elongation at break (EB) of NR and its blends with NBR and CR after ageing can be attributed to this, as all the three elastomers are highly unsaturated. However, these blends exhibited better retention of tensile strength and tear than NR after ageing. NR/CR blend exhibited better resistance than NR/NBR blend especially in the case of tear strength. This is because, compared to NBR, the polymer backbone of CR is more resistant to attack by oxygen due to the deactivating effect of the electrophilic chlorine group. Blends with HNBR showed far better retention, whereas blends with EPDM exhibited excellent resistance towards thermal oxidation as a result of the stable saturated polymer back bone structure of these two elastomers (Burrowes, 2004; Arnis, 2004; Jones *et al.,* 1996). However, the retention of EB was lower than that of NR/HNBR.

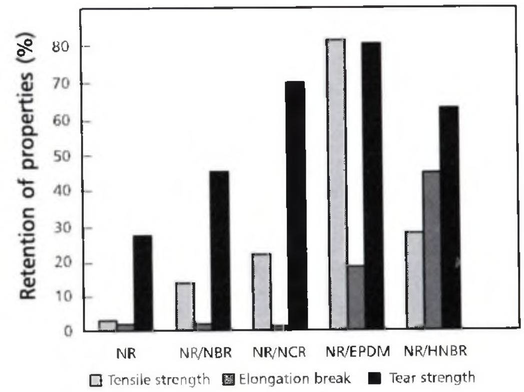


Fig. 2 . Percentage retention of properties after ageing at 150 °C for 24 h.

Oil ageing

Rubber components such as hoses, sub-sea flexible pipes and seals are widely used in the field of oil or gas production and in engineering applications. Organic liquids weaken rubbers by swelling, where as corrosive liquids tend to attack chemically (Robert Campton, 2003; De *et al.*, 2003). Different rubbers withstand such attack to different levels depending on their chemical structure. A highly swollen rubber is often too weak to be useful. NR being non-polar undergoes swelling in petroleum oils and fuels.

The retention of properties of NR and its blends after immersion in ASTM No.2 oil at room temperature for 5 days is shown in Figure 3.

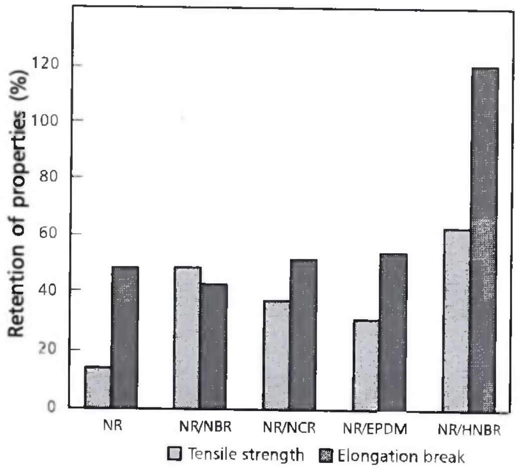


Fig. 3. Retention of properties after ageing in ASTM oil No: 2 for 5 days at room temperature.

All the blends showed improved resistance towards oil ageing than pure NR. As expected, blends with NBR and HNBR exhibited very good resistance, due to the presence of the polar acrylonitrile group on them. Blends with CR and EPDM showed comparatively poor resistance as evident in the photographs of the swollen samples (Fig. 4).

The percentage swell of NR and the blends in ASTM oil Nos. 1, 2 and 3 at three different temperatures *viz.,* 28, 70 and 100°C for 5 days are presented in Table 4. NR exhibited the least resistance and even dissolved in the oils at higher temperature. This is due to its non-polar nature. Among the blends, blend of NR with

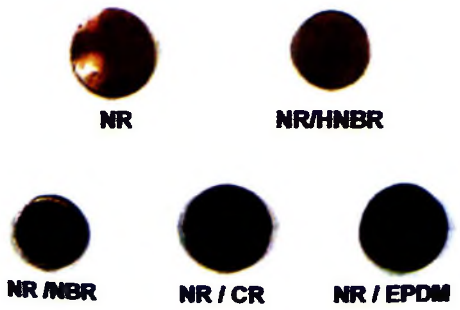


Fig. 4. Photographs of swollen samples of NR and its blends immersed in ASTM No: 2 oil for 5 days at room temperature

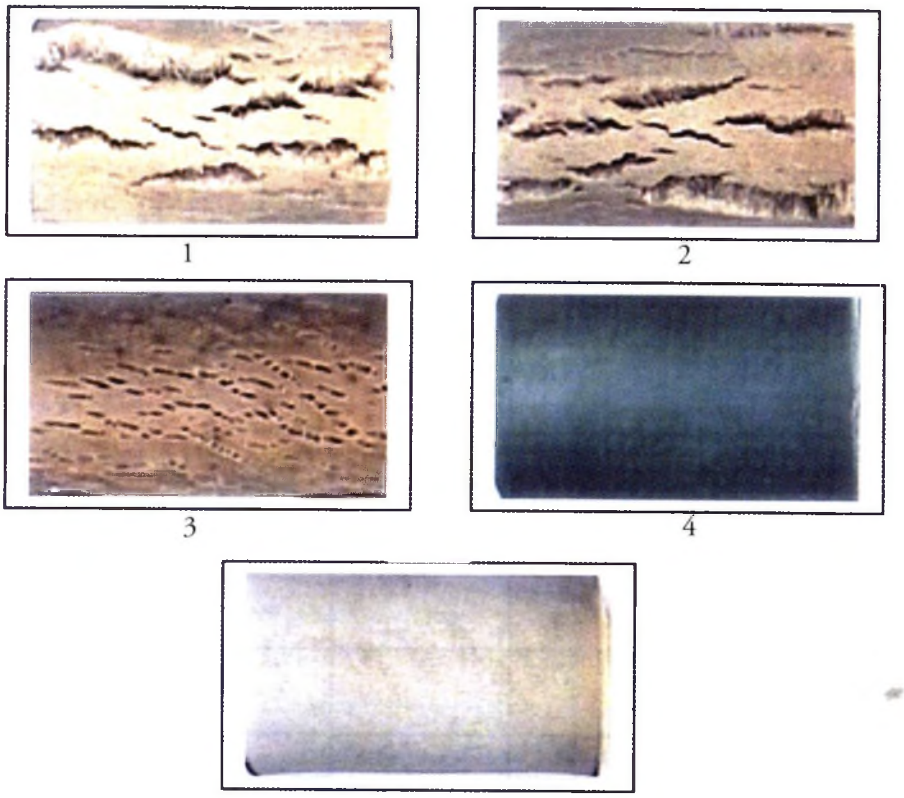
Table 4. **Percentage swelling of NR and its blends in ASTM oils for 5 days**

Temperature, °C	ASTM Oil No.	NR	NR/NBR	NR/CR	NR/EPDM	NR/HNBR
28	1	47.5	16.1	24.9	30.5	15.6
	2	71.8	22.1	39.6	44.5	22.3
	3	180.7	63.9	147.4	151.9	54.7
70	1	126.9	42.8	95.5	124.0	33.6
	2	207.6	77.7	141.7	184.9	68.2
	3	285.8	115.2	272.2	283.2	101.9
100	1	Dissolved	83.4	94.0	182.9	79.5
	2	”	115.7	138.9	204.3	99.8
	3	”	198.0	279.0	409.0	143.0

EPDM showed lower resistance as EPDM also contains no polar group. Blends with NBR and HNBR exhibited very good oil resistance. NR/HNBR blend gave better resistance at higher temperature than NR/NBR blend due to the excellent heat ageing resistance of HNBR (Gomez *et al.*, 2003; Takashi *et al.*, 2002). Selective hydrogenation of the C=C bonds in HNBR gives excellent resistance to heat ageing, while the nitrile group provides very good oil/fuel resistance (Sharon *et al.*, 2005). NR/CR blend exhibited better resistance than NR and NR/EPDM blend since CR also contains Cl as polar group.

Ozone ageing

One of the main types of degradation of rubber products under natural conditions is caused by atmospheric ozone generated in nature by electrical discharge and also by solar radiation in the stratosphere. Very low quantity (a few pphm) of ozone in air can cause cracking on surfaces which spoils the appearance and may destroy usefulness of the products. Ozonation and antioxident efficiency of rubbers and their blends has been extensively studied (Avirah *et al.*, 1995; Ismail *et al.*, 2001). The cracking is the result of the rapid reaction of ozone with the olefinic double bonds to



1 2 3 4 5

Fig. 5. Vulcanizate surfaces after 40 h exposure to ozone atmosphere. 1. NR and 2. NR/NBR, 3. NR/CR, 4. NR/EPDM, 5. NR/HNBR

form an ozonide ring. The scission of the ring produce surface cracks when the rubber is under stress. The cracks formed on the surface perpendicular to the applied stress, is propagated catastrophically into the interior resulting in failure of the product.

The optical photographs of the ozone-exposed surfaces of NR and its blends in an ozone chamber at 50 pphm ozone concentration at 38°C for 50 h are shown in Figure 5. Within the first two hours cracks were formed on the surfaces of NR and NR/NBR blend and the deepening of the cracks was very fast. Cracks were developed only after 16 h on the NR/CR blend and propagated slowly, whereas blends of NR with EPDM and HNBR showed no cracks up to 50 h of exposure. This indicates the improved ozone resistance of the NR blends with the saturated rubbers.

Exposure to Υ-radiation

The tensile properties of the blends after Υ irradiation of all the vulcanizates showed a reduction (Table 5). It was observed that the properties drastically reduced in NR and NR/CR blends, probably due to the cleavage of double bonds. NR/EPDM exhibited higher retention of properties while NR/NBR and NR/HNBR showed similar retention. Higher degradation occurred on prolonged irradiation (Vinod *et al.,* 2002). However, NR/HNBR showed improved modulus and elongation, indicating additional crosslinking along with degradation.

CONCLUSION

Blends of NR with speciality elastomers like CR, NBR, EPDM and HNBR exhibited improved ageing characteristics, but inferior tensile properties compared to NR. Among these, NR/HNBR blend exhibited a combined ageing resistance towards heat, oil, ozone and radiation. NR/EPDM blend even though had excellent resistance towards ozone and heat ageing, showed very poor resistance towards oil ageing and had very low tensile properties. NR/NBR blend showed better oil and radiation resistance, but very poor resistance towards heat and ozone. Blend of NR/CR showed only slight improvement towards heat, oil and ozone resistance.

Table 5. **Tensile properties of vulcanizates of NR and blends after Υ irradiation**

Property	NR	NR/NBR	NR/CR	NR/EPDM	NR/HNBR
Radiation at 15 M rad					
Tensile strength, MPa	7.6	12.7	6.7	4.0	12.5
Elongation at break, %	510	560	535	350	350
Modulus, 100%, MPa	1.07	1.64	0.97	1.37	1.53
Modulus, 300%, MPa	2.28	3.81	1.75	3.03	2.99
Radiation at 25 M rad					
Tensile strength, MPa	2.8	7.6	3.6	3.1	7.9
Elongation at break, %	415	500	390	385	410
Modulus, 100%, MPa	0.64	0.99	0.72	0.92	1.81
Modulus, 300%, MPa	1.47	2.47	2.38	2.12	3.46

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