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STUDIES ON BLENDS OF NATURAL RUBBER AND 1, 2-POLYBUTADIENE

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Blends having different proportions of natural rubber and thermoplastic 1,2-polybutadiene were prepared and evaluated for processing characteristics, technological properties, ageing and ozone resistance. The results indicated that the cure rate index of the blends decreased as the proportion of 1,2-polybutadiene in the blend increased. Better technological properties were obtained for the blends which contained a higher proportion of natural rubber. However, ageing and ozone resistance were better for the blends which contained a higher proportion of 1,2-polybutadiene. The reinforcing effect of silica in these blends was similar to its effect in normal rubber compounds.

Key words:-Natural rubber, Blends, 1,2-polybutadiene, Cure rate index, Ageing resistance, Ozone resistance, Silica.

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INTRODUCTION

Polymer blends are usually heterogenous in nature because of the thermodynamic incompatibility between the components. At least in some cases, such as thermoplastic-elastomer blends, many useful properties result from the thermodynamic incompatibility of the components. Blending of two elastomers or an elastomer and a thermoplastic material is usually done with specific objectives such as enhancement of physical properties and improvement of resistance to the action of heat, oxygen and ozone and of processing characteristics. Blending of natural rubber (NR) or styrene-butadiene rubber (SBR) with ethylene-propylene diene rubber (EPDM) or blending of nitrile rubber with polyvinyl chloride (PVC) is reported to improve ozone resistance (Almond, 1962; Ambelang *et al.*, 1969; Buckler and Harris, 1955; Mathew, 1984, 1988).

Natural rubber has excellent physical properties and very good processing characteristics. But this polymer lacks resistance to action of heat, oxygen and ozone and hence has only limited application in areas where such conditions prevail for long periods. 1,2-polybutadiene (1,2-PB), which is a thermoplastic elastomer, offers very good processing characteristics and excellent resistance to ozone due to its crystalline nature and saturated backbone structure respectively. It can also be vulcanized with sulphur or peroxide, like natural rubber. Hence in the present study, blends of NR and 1,2-PB were prepared and evaluated for their cure characteristics, technological properties and ageing and ozone resistance.

EXPERIMENTAL

Materials

NR used for the study was ISNR 5 (light

colour) grade rubber. 1,2–PB used was JSR RB 820 manufactured by Japan Synthetic Rubber Company. All the other ingredients used were of commercial grade. The characteristics of the base polymers are given in Table 1.

Table 1. **Characteristics of base polymers**

Characteristics	Natural rubber	1, 2–Polybutadiene
Molecular weight ($\bar{M}w$)	7,80,000	1,00,000
Plasticity retention index (PRI)	75	—
Initial plasticity (Po)	59	—
Melt flow index (MFI) (150°C, 2.16 kg, g/10 min)	—	3
Melting point (°C)	—	80
Crystallinity (%)	—	25
Density (g/cm^3)	0.93	0.91

Preparation of blends

Blends were prepared in a laboratory model Intermix (Shaw Intermix KO) set at a temperature of 90°C and a rotor speed of 40 rpm, the blending time being 3.5 min. The blends contained 0, 10, 20, 30, 40, 50, 60, 80 and 100 per cent of 1,2–PB (designated as Ao, A, B, C, D, E, F, G and H, respectively). The silica filled blends are designated as AoS, AS, BS etc. The blends were compounded in a two roll laboratory mill as per the test recipes given in Table 2. An efficient vulcanization system suggested by Kuriakose (1986) was chosen. The mill rolls were heated to soften those blends which contained a higher proportion of 1,2–PB. The compounded blends were cured for the respective optimum cure time at 150°C in a steam heated hydraulic press to get the test samples.

Table 2. **Formulation of the mixes**

Ingredients	Ao, A, B, C, D, E, F, G, H	AoS, AS, BS, CS, DS, ES, FS, GS, HS
Polymer	100.00	100.00
Zinc oxide	5.00	5.00
Stearic acid	1.00	1.00
Phenyl - β -naphthyl amine	1.00	1.00
N-Cyclohexyl benzothiazyl sulphenamide	1.50	1.50
Tetramethyl thiuram disulphide	1.75	1.75
Sulphur	0.50	0.50
Silica (Ultrasil VN$_3$)	—	39.00
Diethylene glycol	—	2.00
Naphthenic oil	—	3.50

Testing

The basic physical properties were evaluated as per the respective ASTM test procedures. The volume fraction of polymer in toluene swollen sample (Vr) was estimated as per the procedure described by Ellis and Welding (1964).

Ozone resistance was ascertained adopting the quantitative method described by Wilchinsky and Kresge (1974). Tapered test samples were kept elongated by the application of a load for 24 h and then exposed to ozone at a concentration of 50 pphm for 24 h at 40°C. The critical stress, σ_c, was determined directly from the applied load and the cross sectional area at the critical boundary and the critical strain, ϵ_c, was calculated from the overall elongation and the position of the critical boundary. The critical elastic stored energy density, Wc, which is a quantitative measure of the resistance of the polymer to ozone attack was calculated using the following relationship from the classical theory of rubber elasticity:

$$W_c = \tfrac{1}{2}\, \sigma_c\, \epsilon_c\, (\lambda_c^2+2)/(\lambda_c^2 + \lambda + 1) \quad (1)$$

where λ_c is the extension ratio $(1 + \epsilon_c)$ at the point of critical strain.

RESULTS AND DISCUSSION

The technological properties of the unfilled blends are given in Table 3 and those of the silica filled blends in Table 4. Figure 1 shows the trend in ageing resistance of the unfilled and silica filled blends expressed as percentage retention of tensile strength and elongation at break after ageing at 100°C for 4 days. Figure 2 shows the critical elastic stored energy density which is a quantitative measure of the resistance to ozone attack.

Table 3. **Physical properties of unfilled blends**

Properties	Sample number								
	Ao	A	B	C	D	E	F	G	H
Cure time, t_{90} at 150°C, (Minutes)	7.0	7.0	7.5	8.0	9.0	10.0	10.5	11.75	16.5
Cure rate index ($100/t_{90}$—t_{s2})	33.00	30.76	28.57	26.66	22.22	18.18	17.39	16.66	10.52
Modulus 300% (MPa)	1.88	2.34	2.75	3.27	3.67	4.37	5.12	6.80	8.60
Tensile strength (MPa)	21.50	20.80	20.90	17.10	14.30	8.05	6.06	9.10	15.20
Elongation at break (%)	841	818	785	762	643	487	339	367	397
Hardness (Shore A)	40	43	47	52	57	62	68	77	82
Compression set 22 h, 70°C (%)	15.3	17.9	19.9	25.4	28.3	32.5	46.8	52.5	63.9
Goodrich heat build-up at 50°C, ΔT (°C)	7	8	11	13	17	17	20	B.O.	B.O.
Tear strength (kNm^{-1})	31.2	34.0	37.9	42.9	44.1	47.9	50.7	56.6	68.8
DIN abrasion loss, 10N load (mm^3)	207.2	202.6	188.9	194.5	204.8	250.8	229.9	264.6	226.5
Volume fraction of polymer (Vr)	0.2011	0.2004	0.1878	0.1842	0.1802	0.1776	0.1727	0.1709	0.1775

B.O. – Blown out

Table 4. **Physical properties of silica-filled blends**

Properties	Sample number								
	AoS	AS	BS	CS	DS	ES	FS	GS	HS
Cure time, t_{90} at 150°C (minutes)	2.5	2.6	3.0	3.0	3.75	4.0	5.75	6.0	9.0
Modulus 300% (MPa)	6.30	6.80	6.95	6.95	7.05	7.30	7.40	8.55	9.90
Tensile strength (MPa)	26.15	25.16	23.43	21.20	18.35	17.96	14.85	13.50	15.60
Elongation at break (%)	574	533	529	516	507	500	446	365	333
Hardness (Shore A)	66	70	74	76	80	83	85	87	89
Compression set 22 h, 70°C (%)	37.85	40.81	47.17	53.16	58.36	62.58	70.96	78.41	81.44
Goodrich heat build-up, at 50°C, △ T (°C)	36	40	43	43	49	51	58	B.O.	B.O
Tear strength (kNm^{-1})	90.35	92.30	98.85	88.50	75.35	79.00	76.10	73.40	77.50
DIN abrasion loss, 10N load (mm^3)	136.7	139.5	131.2	132.2	139.8	141.5	152.7	158.5	165.0

B.O.—Blown out

Cure characteristics of the blends

The cure time of the blends increased with increase in the proportion of 1,2–PB. The cure rate index showed a decreasing trend with increase in 1,2–PB content in the blend. The cure rate index of the compound which contained only 1,2–PB (Compound no. H) was about one third of that of compound Ao which contained only NR. This is due to the fact that in 1,2–PB the double bond is present in the side group and there is no strong electrophillic group on the main chain to activate the double bond towards electrophillic reaction, like the methyl group in the NR chain. Even though Vr values of the blends may not be directly proportional to crosslink density due to the differences between the polymer/solvent interaction parameters of the components of the blend, these values can be considered indicative of the extent of crosslinking. It is observed that the extent of crosslinking also decreased as the proportion of 1,2–PB in the blend increased as indicated by lower Vr values. When the proportion of 1,2–PB in the blend was 50 per cent or more (blends E to H), there was no further significant change in the Vr values.

Physical properties

The data given in Table 3 demonstrate a regular increase in properties such as modulus, hardness, compression set, heat build-up and tear strength of the vulcanizates with an increase in the proportion of 1,2 – PB in the blend. This observation can be explained based on the fact that 1,2–PB has about 25 per cent crystallinity. Also, this material can form a continuous phase in the blend even when its proportion is, lower, since its molecular weight is lower than that of NR (Table 1) and hence has a lower melt viscosity at the temperature of processing. The regular increase in the properties such as hardness, modulus and tear strength can be due to the combined effect of the above basic

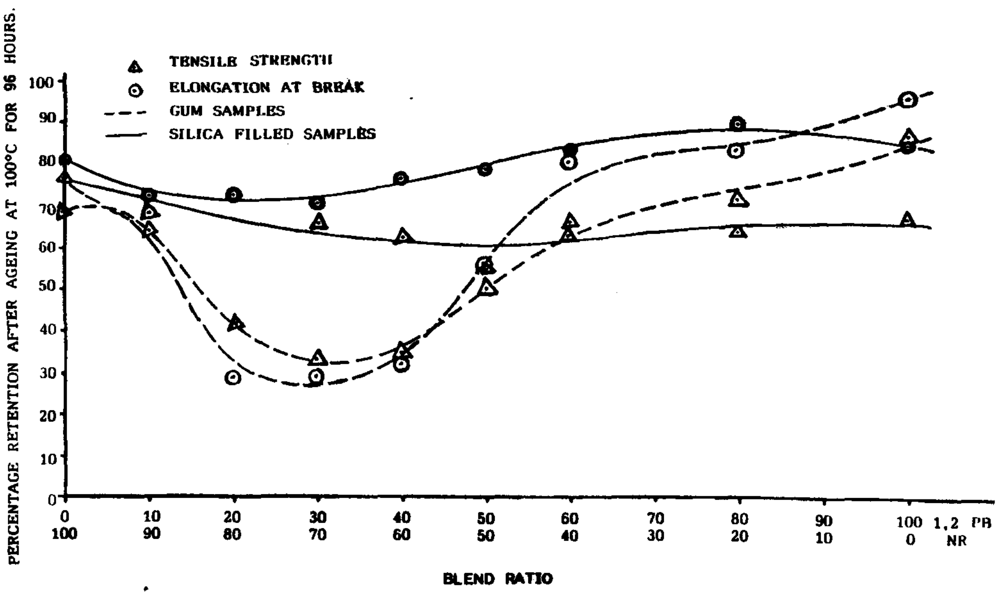

Fig. 1. Effect of blend ratio on ageing resistance.

properties of 1,2–PB. The increase in the compression set and heat build-up in proportion to the 1,2–PB content is due to the lower extent of crosslinking as is evidenced by Vr values, which are lower for the blends containing higher proportions of 1,2–PB.

Properties such as tensile strength, elongation at break and abrasion resistance did not follow a regular trend following the blend ratio. Tensile strength and elongation at break were higher for the vulcanizates which contained a higher proportion of NR in the blend. These properties decreased sharply as the proportion of NR in the blend was reduced beyond 50 per cent (blends E to G). Abrasion resistance of the vulcanizates E to H was also lower when compared to that of the vulcanizates A to D. These observations indicated that there is a change in the morphology with variation in the composition of the blends. When the proportion of NR is reduced to less than 50 per cent, it can remain only as a dispersed phase in the blend due to its higher viscosity. In contrast 1, 2–PB can form a continuous phase even at proportions lower than 50 per cent due to its lower melt viscosity. The extent of cure undergone by each component in the blend can also be different as indicated by the widely different cure rate indices of the compounds made from pure components. Therefore natural rubber, which remained as the dispersed phase in blends E to G, would have undergone a higher extent of cure compared to 1, 2–PB because of the higher rate of cure of NR, had there been equal distribution of the curing agents between the two phases. A higher extent of cure can lead to less deformation of the dispersed particles which, in turn can act as stress raisers in the tensile mode of failure.

Effect of precipitated silica on technological properties

Addition of precipitated silica imporved properties such as modulus, tensile strength, hardness, tear strength and abrasion resi-

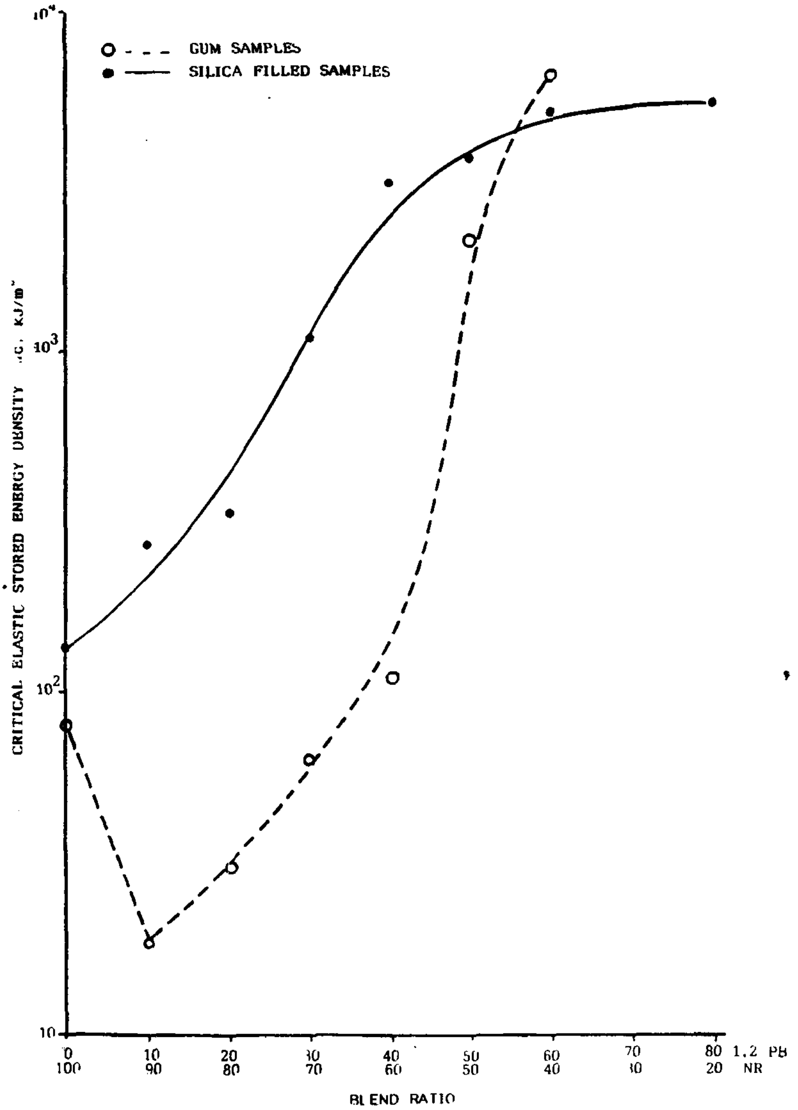

Fig. 2. Effect of blend ratio on ozone resistance.

stance of the blends substantially. The data given in Table 4 show that the improvement in the above properties was evident at all blend ratios. However, the enhancement of tensile properties of the compound H, which contained only 1,2-PB, was only marginal. Properties such as elongation at break, compression set and heat build-up of the blends were adversely affected by the addition of silica. This behaviour is associated with the high reinforcing action of silica, like that occurring in normal rubber compounds.

Ageing resistance

The retention of tensile strength and

elongation at break of the blends after ageing at 100°C for 96 h is shown in Fig. 1. For the gum samples, the retention of both tensile strength and elongation at break, decreased drastically with the addition of 1,2-PB to NR upto the level of about 50 per cent. At higher proportions of 1,2-PB the ageing resistance of the blends improved as indicated by the higher retention of elongation at break and tensile strength of such blends. In the case of the silica-filled samples the same trend was observed for the retention of elongation at break. However, in the case of tensile strength retention was the lowest for the blend which contained equal proportions of NR and 1,2-PB. It can also be observed that for the silica filled blends which contained a higher proportion of NR, retention of tensile strength and elongation at break was much higher than that of the respective gum compounds.

Ozone resistance

Ozone resistance of elastomers is usually determined qualitatively by exposing test samples, which are extended beyond their critical strain, to ozonised air having a specific ozone concentration and then making periodic observation for initiation of cracks. Quantitative determinations are much more reliable and ozone resistance in terms of Wc obtained for the gum and silica-filled blends are shown in Figure 2. It is observed that for the unfilled blends, there is a sudden drop in ozone resistance with the addition of 1,2-PB upto the level of about 50 per cent. However, as the proportion of 1,2-PB in the blend increased beyond 40 per cent, Wc values increased sharply. In polymer blends the component which has lower melt viscosity tends to form an outer sheath under shear during processing operations (Van Oene, 1978) and such behaviour can be expected. In the present case, 1,2-PB which has a lower melt viscosity compared to NR, can form an outer surface layer when its proportion in the blend exceeds about 40 per cent. Since 1,2-PB is having a saturated backbone structure, it is highly resistant to the attack by ozone. Hence the formation of a protective sheath by 1,2-PB when its proportion was more than 40 per cent, may be the reason for the sharp increase in Wc value and the resistance to ozone attack of such blends. The higher Wc values of the silica-filled blends are due to the higher critical stress values of these blends whose moduli are also much higher.

CONCLUSIONS

The following conclusions emerge from the investigations:

1. In blends consisting of NR and 1,2-PB, cure rate index decreases as the proportion of 1,2-PB in the blend is increased.
2. For better technological properties, blends containing a higher proportion of NR are to be used.
3. Ageing and ozone resistance are better for blends containing higher proportions of 1,2-PB.
4. The reinforcing action of silica in NR-1,2-PB blends is similar to its action in normal elastomers and use of silica improves the technological properties of the blends to a great extent.

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