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STUDIES ON OZONE RESISTANCE OF NATURAL RUBBER — ETHYLENE/PROPYLENE RUBBER BLENDS

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The ozone resistance of blends of natural rubber (NR) and ethylene/propylene rubber (EPM) was quantitatively assessed in terms of critical stress-strain parameters. The effects of blend ratio and addition of carbon black and china clay on ozone resistance were also studied. It is observed that resistance of NR vulcanisates to ozone cracking is remarkably improved by blending it with EPM rubber. A blend ratio in the range of 80 : 20 to 70 : 30 NR : EPM is found to give adequate protection against ozone attack. Addition of high abrasion furnace (HAF) black improves ozone resistance of NR and the blends. Blending of HAF black masterbatches of the two polymers is beneficial only when the proportion of EPM is more than 30 parts per hundred rubber (phr). Addition of china clay reduces ozone resistance of natural rubber and the blends drastically.

Key words – Ozone resistance, Polymer blends, NR/EPM blends, Masterbatch, Carbon black, China clay, Critical stress, Critical strain, Critical stored elastic energy density.

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INTRODUCTION

Among the external factors causing deterioration of rubber products, the most important ones are oxygen and ozone. Both these gases are present in the atmosphere, although the concentration of the latter is usually very low. While attack by oxygen is relatively slow and activated by heat, ozone attack is rapid. Hence even very low concentrations of ozone can cause cracks in rubber under strain. The degree of unsaturation of an elastomer is the most important factor determining its susceptibility to ozone attack.

There are several methods to protect an elastomer from ozone attack. The most common is the use of petroleum wax. Waxes give adequate protection as long as the product is subjected only to static conditions of exposure. Under dynamic conditions, wax film, being inextensible, ruptures leaving the elastomer unprotected (Lederer and Fath, 1981). Another method is the use of flexible coatings (Cutts and Wheelans, 1974). Polyurethane paints are the most promising among these. But both these methods provide only a physical barrier against ozone and are not suitable for dynamic applications. Hence the use of chemical antiozonants becomes more relevant as far as dynamic applications are concerned (Lake, 1970). But the disadvantage with chemical antiozonants is that they are highly staining and are likely to be lost during processing and service. Blending unsaturated elastomers like natural rubber with ozone inert rubbers such as EPDM, to improve ozone resistance, has already been reported (Mathew, 1984). However, high proportions of EPDM are required for adequate levels of protection. When high proportions of EPDM are blended with NR, some of the physical properties like tensile strength, tear strength etc. are adversely affected, possibly due to the lack of full compatibility and the difference in the cure rate of the two polymers. If a more saturated polymer like EPM is used, it is likely that higher levels of protection could be achieved by blending with lower proportions of the saturated polymer. Although some work has already been reported (Andrews, 1966; Joseph and O'Mahoney, 1970), detailed studies on the effect of fillers like carbon black and china clay in such blends have not been made. The method of addition of black is also reported to be affecting ozone resistance of these blends (Mathew, 1984). In the present study the effects of fillers like china clay and HAF black and the method of addition of the black on the ozone resistance of NR/EPM blends are quantitatively assessed.

EXPERIMENTAL

MATERIALS

The natural rubber used in the present study was ISNR-5. The ethylene propylene rubber (EPM) was Keltan 512 of DSM Holland. HAF (N-330) carbon black was supplied by M/s Philips Carbon Black Ltd., Durgapur. Commercial grades of china clay and dicumyl peroxide (DCP, 40 per cent activity) were used. The composition of the mixes are given in Table 1.

Table 1. Composition of Mixes

	A1 — A6	B1 — B6	C1 — C6	D1 — D6
* Polymer	100	100	100	100
HAF black	..	50	50	..
China clay	..	..	..	50
Naphthenic oil	..	5	5	5
Dicumyl peroxide	6.25	6.25	6.25	6.25

* Mixes A1 — A6	were 100 : 0, 95 : 5, 90 : 10, 80 : 20, 70 : 30 and 60 : 40 NR : EPM blends.
* Mixes B1 — B6	were 100 : 0, 95 : 5, 90 : 10, 80 : 20, 70 : 30 and 60 : 40 NR : EPM blends in which black was added to the pre blended polymers.
* Mixes C1 — C6	were 100 : 0, 95 : 5, 90 : 10, 80 : 20, 70 : 30 and 60 : 40 NR : EPM blends in which black was added to the individual polymers followed by blending of the masterbatches.
* Mixes D1 — D6	were 100 : 0, 95 : 5, 90 : 10, 80 : 20, 70 : 30 and 60 : 40 NR : EPM blends in which china clay was added to the pre-blended polymers.

MIXING AND MOULDING

The mixes were prepared on a laboratory size two roll mixing mill (15 cm x 30 cm) at a friction ratio of 1 : 1.25. Mixting time and temperature were controlled during the studies. The viscosity of NR was first reduced by mastication and the two rubbers were blended at the same viscosity. For masterbatch blending, carbon black was added to the individual rubbers and the black master-batches thus prepared were blended in appropriate proportions followed by addition of the other ingredients.

Optimum cure time of the mixes were determined using a Monsanto Rheometer R–100 at 150°C and the mixes were vulcanised into 2 mm sheets using a steam heated hydraulic press.

PHYSICAL TEST METHODS

The tensile properties and tear strength of the vulcanisates were determined using a Zwick Universal Testing Machine (Model 1474), as per ASTM D : 412–75 Method A.

OZONE RESISTANCE

Ozone resistance of the samples was measured in terms of critical stress-strain parameters by the method developed by Andrews (1966) and later modified by Wilchinsky and Kresge (1974). A tapered specimen was cut from the vulcanised sheet using a special type of die. The geometry of the sample is given in Fig. 1A. Bench-

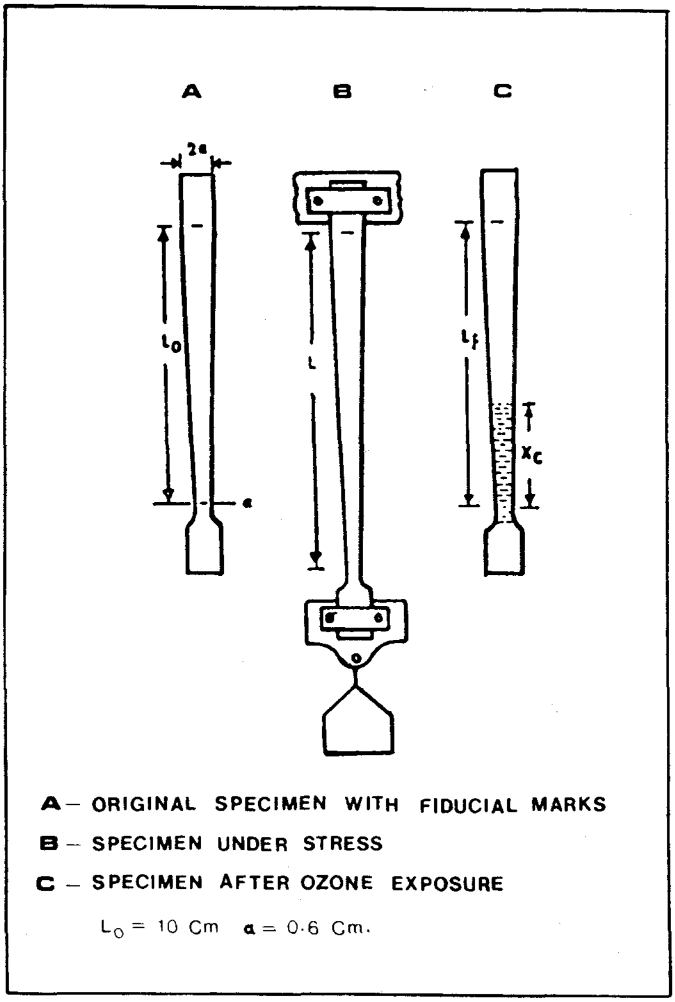

Fig. 1. Geometry of the ozone test specimen

marks were made 10 cm apart (Lo) and specimen thickness was measured at the ends and the middle of the tapered section. The specimen was suspended by one end on a portable rack and a selected weight was hung at the lower end with the aid of a clamp as shown in Fig. 1B. After the specimen had been under tensile stress for 16 hours the extended length (L) was measured. The rack holding the specimen was then placed in the ozone chamber (Mast model 700–1) for 24 hours. The concentration of ozone was maintained at 50 pphm and the temperature at 37.5°C. After ozone exposure, the load and clamps were taken out. Measurement of length Xc to the boundary of cracked zone and distance Lf between the benchmarks were made. The latter is longer than Lo due to irreversible creep. The critical stress (σc) was determined directly from the experimental data by:

$$\sigma_c = \frac{F}{a t_c\left(\frac{1+X_c}{Lf}\right)} \quad \ldots\ldots \quad (1)$$

where 'a' is the width of the undeformed specimen at the narrow end ($X = 0$) of the taper and t_c is the thickness at X_c obtained by interpolation between two thickness measurements made at the two ends and at the middle of the specimen. The critical strain (ϵ_c) was measured using the approximation:

$$\epsilon_c = \left(1.42 - \frac{1.42}{\lambda av}\right) \Big/ \left[(X_c/L_o) - 0.42 + \frac{1.42}{\lambda av}\right] \quad \ldots\ldots \quad (2)$$

where λav is the average elongation. The critical elastic stored energy density was calculated from σ_c and ϵ_c by the following relationship from the classical theory of rubber elasticity:

$$W_c = \tfrac{1}{2}\sigma_c \epsilon_c (\lambda_c+2)/(\lambda_c^2+\lambda_c+1) \quad \ldots\ldots \quad (3)$$

Finally the elastic modulus E was obtained from:

$$E = \lambda_c \sigma_c / \epsilon_c \quad \ldots\ldots \quad (4)$$

RESULTS AND DISCUSSION

The stress-strain properties and the ozone resistance in terms of critical stress-strain parameters were evaluated for the unfilled and filled NR/EPM blends.

1. UNFILLED VULCANISATES

As the effect of blending polymers can be more appropriately determined in unfilled compounds, blends of varying NR/EPM ratios have been examined for their physical properties with special reference to ozone resistance. A series of NR/EPM blends were prepared from 100 : 0 to 60 : 40 NR/EPM (A1–A6). Since it is believed that adequate protection against ozone attack could be realised by 40 parts of EPM, proportions higher than this were not included in the present study.

As EPM is fully saturated, dicumyl peroxide was used as the vulcanising agent. The cure characteristics and physical properties of these vulcanisates are given in Table 2. As expected, optimum cure time and cure rate index are not affected much by the blend ratio. There is an increase in the maximum torque as the proportion of EPM in the blend is increased. However, a corresponding increase in modulus and tensile strength is not observed, although some of the blends containing EPM show higher modulus and higher tensile strength than natural rubber. Tear strength is found to remain rather unchanged with the addition of EPM.

Figs. 2, 3 and 4 show the effect of blending of EPM on critical stress (σ_c), critical strain (ϵ_c) and critical stored elastic energy density

Table 2. Cure Characteristics and Physical properties of Unfilled Mixes

MIX	A1	A2	A3	A4	A5	A6
Optimum cure time at 150°C (Minutes)	50	56	48	55	53	51
Cure rate index	1.88	1.92	1.78	1.64	1.64	1.56
Maximum torque (LB-IN)	60	63	63	65	68	71
300% Modulus (MPa)	2.2	2.5	1.9	3.0	2.3	2.8
Tensile strength (MPa)	8.0	7.7	8.9	7.4	6.9	5.3
Elongation at break (%)	587	552	554	551	470	362
Tear strength (kN/m)	26.4	22.9	25.1	23.7	22.9	22.4

(W_c), respectively of the vulcanisates. It is seen that all the above critical stress-strain parameters are improved progressively with increase in the proportion of EPM. Critical stored elastic energy density is the best criterion to describe the ozone resistance of rubber vulcanisates. It is seen that there is almost a tenfold improvement in W_c by the addition of 20 parts of EPM. However, the author has reported in an earlier work (Mathew, 1984) that in the case of NR/EPDM blends, by the addition of 30 parts of EPDM, Wc is raised only by three times. This shows that EPM is much more effective than EPDM in improving ozone resistance of NR. Fig. 3 shows a fairly rapid increase in ϵ_c beyond 20 phr, whereas it is evident from Fig. 4 that there is an abrupt increase in W_c beyond 20 phr of EPM. This indicates that addition of about 30 phr of EPM in NR gives adequate protection against ozone attack. As is evident from Table 3, elastic moduli of these vulcanisates is found to increase slowly with increase in the proportion of EPM. This correlates better with the increase in maximum torque of these vulcanisates as given in Table 2.

Table 3. Elastic Moduli of Mixes

MIX	*Elastic Modulus E (MPa)*	MIX	*Elastic Modulus E (MPa)*
A1	0.0141	C1	0.0411
A2	0.0177	C2	0.0327
A3	0.0165	C3	0.0316
A4	0.0184	C4	0.0266
A5	0.0169	C5	0.0531
A6	0.0191	C6	0.0568
B1	0.0487	D1	0.0145
B2	0.0375	D2	0.0135
B3	0.0386	D3	0.0097
B4	0.0391	D4	0.0124
B5	0.0497	D5	0.0089
B6	0.0543	D6	0.0088

Filled vulcanisates

(a) *Addition of black to pre-blended polymers*

The cure characteristics and physical properties of these vulcanisates (B1–B6)

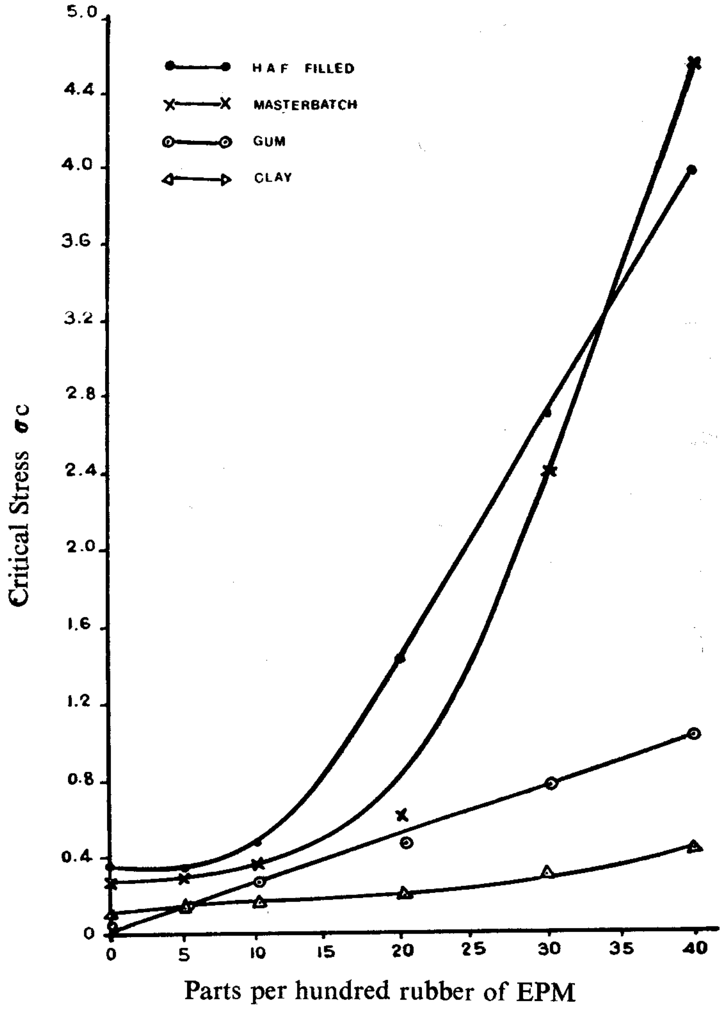

Fig. 2. Effect of blending EPM on the critical stress

are given in Table 4. It is observed that the addition of HAF black slightly decreases the optimum cure time. The modulus remains unchanged by increasing the proportion of EPM, but tensile strength and elongation are found to decrease slightly. There is also a marginal drop in the tear strength.

Addition of black is found to improve ozone resistance of NR and all the blends. As is evident from Figs. 2 and 4, the critical stress and critical stored elastic energy density are found to increase when black is added. Generally, addition of carbon black reinforces rubber vulcanisates and hence its resistance to crack propagation is much higher than that of an unfilled vulcanisate. This explains the higher ozone resistance of the carbon black-filled vulcanisates.

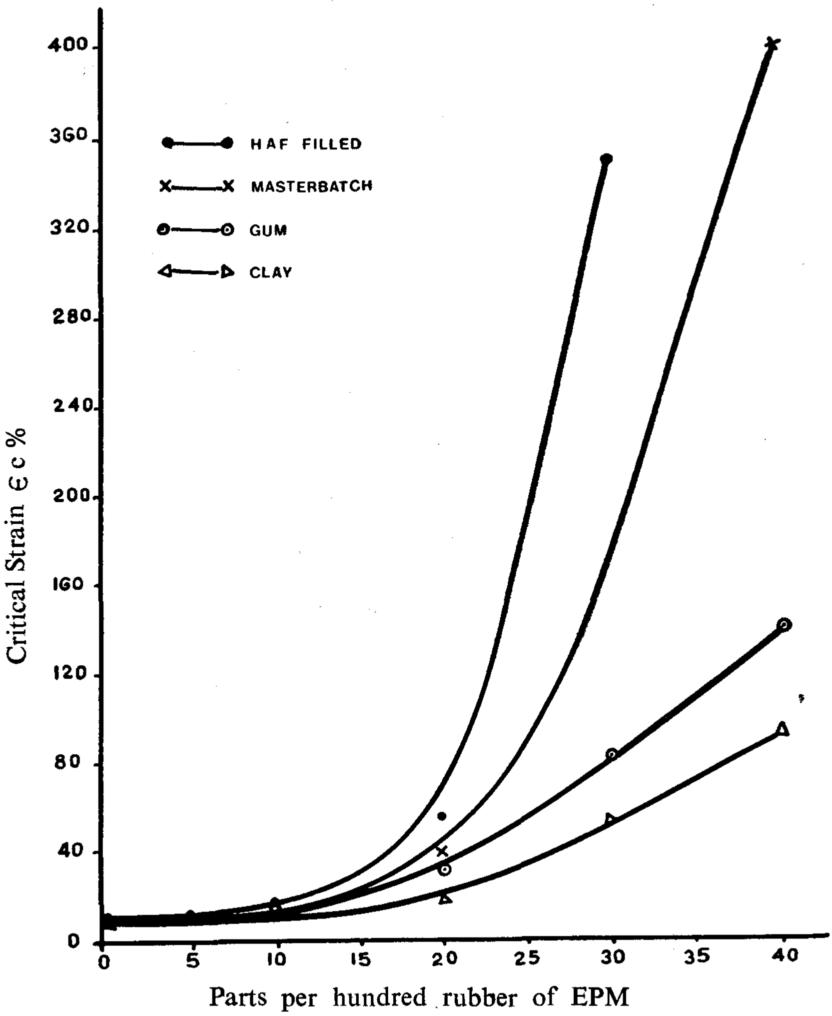

Fig. 3. Effect of blending EPM on the critical strain

Table 4. Cure Characteristics and Physical Properties of HAF Filled Mixes

MIX	B1	B2	B3	B4	B5	B6
Optimum cure time at 150°C (Minutes)	44	41	45	43	45	45
Cure rate index	2.38	2.5	2.33	2.44	2.33	2.38
Maximum torque (LB-IN)	88	88	83	84	90	95
300% Modulus (MPa)	15.7	14.3	14.7	14.0	13.1	14.1
Tensile strength (MPa)	19.0	18.2	16.4	16.6	14.1	15.7
Elongation at break (%)	379	355	344	340	319	326
Tear strength (kN/m)	58.9	61.0	57.0	56.4	52	53

The critical strain of these vulcanisates, where EPM is added beyond 10 parts, is observed to be less than that of the unfilled blends as shown in Fig. 3. This is because the elastic modulus of the filled vulcanisates is much higher than that of the unfilled ones. Therefore, at the same stress, the resultant strain in the black-filled vulcanisates is found to be less. However, in the case of blends having EPM beyond 10 parts, because of the higher ozone resistance which is further improved by black, the vulcanisates are capable of sustaining higher strains without cracking. Therefore, critical strain of the blends containing EPM above 10 parts is increased on the addition of HAF black.

(b) Blending of filler masterbatches

Addition of black to the individual ploymers followed by blending in appropriate proportions is believed to ensure a more uniform distribution of the filler in the polymer blend. The effect of this type of blending

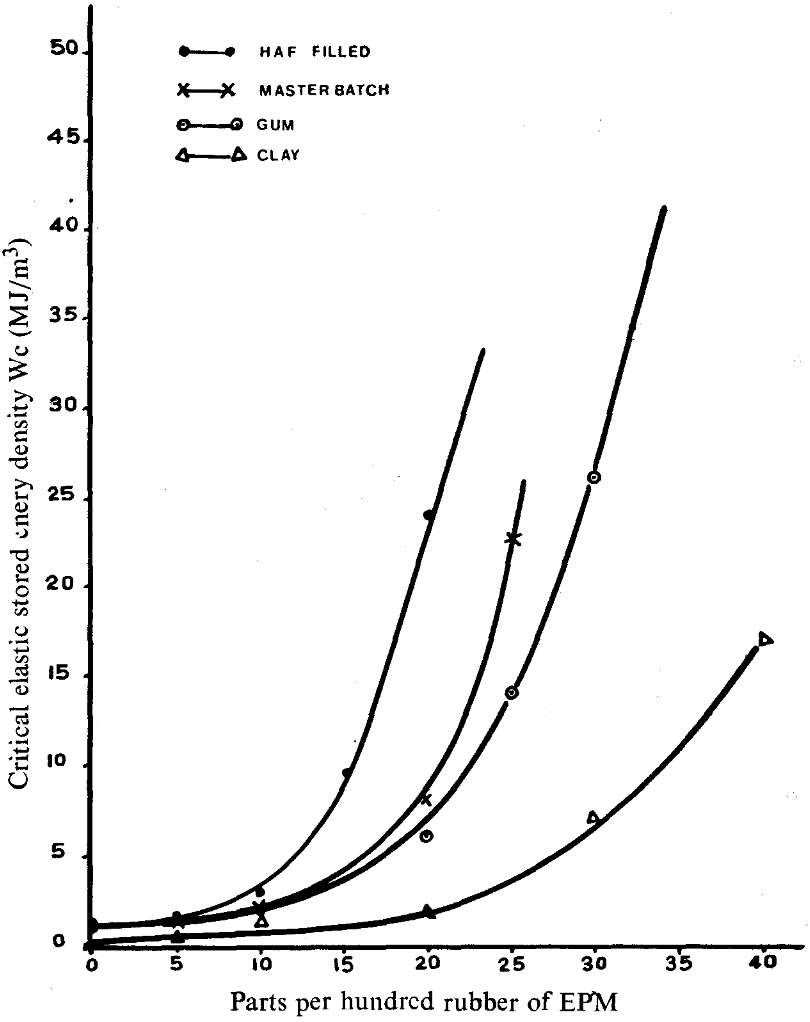

Fig. 4. Effect of blending EPM on the critical elastic stored energy density

was studied. Table 5 shows the cure characteristics and physical properties of these blends (C1-C6). It is seen that cure characteristics are not affected much by the method of addition of black. Modulus and tensile strength show the same tren as in the case of mixes B1-B6. However, elongation is found to increase with the increase in the ratio of EPM.

A comparison of the critical stress-strain parameters of the vulcanisates B1-B6 and C1-C6 shows that these parameters are adversely affected by blending the filler masterbatches upto a blend ratio of 20 phr. But beyond 20 phr, the trend is reversed showing that masterbatch blending is beneficial in realising a higher ozone resistance as the proportion of EPM in the blend is raised.

(*c*) *Addition of china clay to the pre-blended polymers*

The effect of addition of china clay on the ozone resistance of the blend was also studied by adding 50 phr of the filler to the pre-blended polymers and Table 6 shows the cure characteristics and physical properties of these blends (D1-D6). It is found that the cure characteristics are affected by the presence of china clay. Although there is a significant increase in the cure rate index and a corresponding reduction in cure time, there is considerable drop in the maximum torque

Table 5. Cure Characteristics and Physical Properties of HAF-Filled Mixes (Masterbatch)

MIX	C1	C2	C3	C4	C5	C6
Optimum cure time at 150°C (Minutes)	37	37	40	39	40	44
Cure rate index	2.9	2.9	2.6	2.7	2.6	2.4
Maximum torque (LB-IN)	88	88	93	95	93	95
300% Modulus (MPa)	14.9	13.7	14.1	14.7	14.3	9.4
Tensile strength (MPa)	19.9	18.8	18.8	17.4	17.4	15.9
Elongation at break (%)	376	404	443	339	372	425
Tear strength (kN/m)	62.2	63.6	59.9	58.4	53.5	57.5

Table 6. Cure Characteristies and Physical Properties of China Clay-Filled Mixes

MIX	D1	D2	D3	D4	D5	D6
Optimum cure time at 150°C (Minutes)	30	30	32	30	22	21
Cure rate index	3.6	3.6	3.3	3.5	5.0	5.3
Maximum torque, (LB-IN)	50	55	51	44	44	32
300% Modulus (MPa)	3.5	3.5	3.2	3.3	2.6	2.3
Tensile strength (MPa)	11.3	10.2	9.4	7.9	5.8	4.2
Elongation at break (%)	627	594	594	567	565	536
Tear strength (kN/m)	33	29.9	28.9	27.7	23.4	18.3

as clay is added to the polymer blend. It is believed that the acidic nature of china clay causes decomposition of dicumyl peroxide. While a considerable portion of the peroxide is lost as a result of this, it makes the peroxide more active thereby ensuring that the maximum possible degree of crosslinking is attained in a shorter period. In peroxide crosslinking, as the degree of crosslinking is proportional to the quantity of peroxide used, the loss of peroxide through decomposition accounts for a lower maximum torque.

The physical properties of china clay-filled vulcanisates like modulus, tensile strength and tear strength are much inferior to those of the black-filled vulcanisates. This is attributed to the lower degree of crosslinking and to the lower level of rubber-filler interaction.

Figs. 2 and 4 evidently show that ozone resistance of natural rubber and the blends are adversely affected by the addition of china clay. All the critical stress-strain parameters are reduced, even below those of the unfilled vulcanisates. One of the factors for this reduction in ozone resistance may be the lower degree of crosslinking. However, the large particle size and the presence of undispersed clay agglomerates contribute more. These large particles and agglomerates may act as stress raisers when load is applied to the vulcanisates. Therefore, at a given load, the stress around the larger particles and agglomerates are magnified several times thereby causing the critical parameters to be crossed more easily. Hence, it is concluded that in products requiring high levels of ozone resistance, china clay may not be used as a filler.

The following conclusions have been drawn. Resistance of natural rubber vulcanisates to ozone cracking is remarkably improved by blending it with EPM rubber. A blend ratio in the range of 80 : 20 to 70 : 30 NR : EPM is found to give adequate protection against ozone attack. Addition of HAF black improves ozone resistance of NR and the blends. Blending HAF black masterbatches of the two polymers is beneficial only when the proportion of EPM is more than 30 phr. Addition of china clay reduces ozone resistance of natural rubber and the blends drastically.

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REFERENCES

Andrews, E. H. (1966) Resistance to ozone cracking in elastomer blends. *Journal of Applied Polymer Science*, **10**: 47–64.

Cutts, E. and Wheelans, M. A. (1974) Painting of natural rubber with flexible urethane paints. *NR Technology*, **5**(3): 58–62.

Joseph, J. O. and O'Mahoney, J. F. Jr. (1970) EPDM in polymer blends. *Rubber Age*, **102** March: 47–53.

Lake, G. J. (1970) Ozone cracking and protection of rubber. *Rubber Chemistry and Technology*, **43** : 1230–1254.

Lederer, D. A. and Fath, M. A. (1981) Effect of wax and substituted p-phenylenediamine antiozonants in rubber. *Rubber Chemistry and Technology*, **54**: 415–426.

Mathew, N. M. (1984) Scanning electron microscopic studies on ozone cracking of NR and a NR/EPDM blend. *Journal of Polymer Science: Polymer Letters Edition*, **22**: 135–141.

Wilchinsky, Z. W and Kresge, E. N. (1974) A quantitative test for ozone resistance of rubber vulcanisates. *Rubber Chemistry and Technology*, **47**: 895–905.