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VULCANIZATION KINETICS AND PROPERTIES OF NR-EVA BLENDS

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Blends of natural rubber (NR) and ethylene vinyl acetate (EVA), in varying proportions, were prepared with three different cure systems and evaluated for vulcanization kinetics and physical properties. The dicumyl peroxide (DCP) system required a higher energy of activation and longer cure time compared with the sulphur system and the mixed cure system consisting of DCP and sulphur. Most of the important technological properties were better for the blends vulcanized using the mixed cure system compared with those cured with DCP. The blends showed better abrasion resistance, higher hardness, modulus and tear resistance as the proportion of EVA increased.

Key words:- Natural rubber, Ethylene vinyl acetate, Vulcanization kinetics, Cure system, Blends.

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INTRODUCTION

Heterogeneity of elastomer blends results from thermodynamic incompatibility of the components at molecular level. At or below room temperature, elastomer blends remain in separate phases, of which the minor component forms a dispersed phase. Size and distribution of the dispersed phase depend on several factors such as Mooney viscosity, density and solubility parameter of the components, rate of shear during blending and temperature. Properties of elastomer blends depend not only upon the size of the dispersed phase but also on the extent of cure of each. Even if the curative system is selected with utmost care, uneven cure between the phases can occur owing to the difference in the solubilities of the curing agent in each phase and also to the difference in the rates of vulcanization of the components. Many other factors such as uneven distribution of filler and plasticiser also make it difficult to have a blend with balanced properties. Nevertheless, it is common practice to prepare and use blends of two or three elastomers so as to achieve the desired processing characteristics and physical properties. Thus, blending of natural rubber (NR) and ethylene propylene diene rubber (EPDM) or nitrile rubber (NBR), with polyvinyl chloride is reported to improve ozone resistance of NR and NBR respectively (Almond, 1962; Mathew, 1984; Mathew *et al.*, 1988). Blends of NR and butadiene rubber (BR) are reported to have balanced processing characteristics and better abrasion resistance when used for truck tyre tread compounds (Baker and Wallace, 1986). Thermoplastics such as isotactic polypropylene and high density polyethylene improve the processing characteristics of elastomers such as EPDM and NR (Danesi and Porter, 1978; Kuriakose and De, 1985; Akhtar *et al.*, 1987).

Blends of natural rubber and ethylene vinyl acetate rubber (EVA) are being used for many applications such as footwear, cables, etc. But a systematic study on the influence of different cure systems and blend ratios on the kinetics of vulcanization and physical properties of NR–EVA blends is lacking. In this paper the influence of three different cure systems on the above parameters in NR–EVA blends is reported with a view to suggesting a cure system suitable for a particular blend which has the desired physical properties.

EXPERIMENTAL

Materials

NR used for the study was ISNR 5 (light colour). The EVA employed was Exxon 218 (manufactured by Exxon Chemical Company), having vinyl acetate content 18.0 per cent by weight, melt flow index 1.7 g/10 min, density 0.939 g/cm^3 and vicat softening point 64°C. All the other ingredients used were of commercial grade.

Preparation of blends

The blends were prepared in a laboratory model intermix (Shaw Intermix KO) set at a temperature of 80°C and a rotor speed of 60 rpm. NR was masticated for 2.0 min and then blended with EVA for 2.5 min. The final temperature of the blend inside the intermix was in the range of 110°–128° C, depending upon the blend ratio. The blends contained 0, 10,20,30,40,50,60,70,80 and 100 per cent of EVA and were designated A, B, C, D, E, F, G, H, I and J, respectively. The blends were compounded in a two roll laboratory mill as per the test recipes given in Table 1. Compounds which contained sulphur cure system were designated A_1, B_1, C_1, ... etc. and those with DCP as A_2, B_2, C_2, ... etc. Compounds which contained the mixed cure system consisting of sulphur and DCP were designated as A_3, B_3, C_3, ... etc. The dosage of sulphur and DCP in the mixed cure system was not according to the proportion of NR and EVA in the blend because their distribution in these two elastomers can be different. The compounded blends were moulded to optimum cure in a steam heated hydraulic press at 160°C, to get the required test samples. Blends with 50 per cent or more of EVA could not be vulcanized fully with sulphur and hence could not be evaluated for physical properties.

Table 1. **Formulations of the compounds**

Ingredients	Sulphur system	DCP system	Mixed system
Polymer	100.0	100.0	100.0
Zinc oxide	5.0	5.0	5.0
Stearic acid	1.5	1.5	1.5
Styrenated phenol antioxidant	1.0	1.0	1.0
Dibenzothiazyl disulphide	0.8	—	0.8
Dicumyl peroxide (40% active ingredient)	—	4.0	4.0
Sulphur	2.5	—	2.5

Testing

The kinetics of vulcanization was evaluated using a Rheometer 100. The range of temperature selected was 160°C to 190°C. The angle of oscillation of the rotor was 3° and the frequency 100 cycles per minute. The physical properties were determined as per the relevant ASTM test procedures.

RESULTS AND DISCUSSION

A general equation for the kinetics of a first order chemical reaction can be written as

$$\ln (a - x) = - kt + \ln a \qquad \text{.........} (1)$$

where a = initial reactant concentration

x = reacted quantity at time 't', and

k = first order reaction rate constant

The rate of crosslink formation is usually monitored by measuring the torque developed during the course of vulcanization by using a curometer and the torque values thus obtained are proportional to the modulus of the rubber. Hence if a physical property such as modulus is being measured rather than the change in reactant concentration, then the following substitutions can be made

$$(a - x) = (M_x - M) \qquad \text{......} (2)$$

$$a = (M_x - M_0) \qquad \text{......} (3)$$

where M_α = maximum modulus,

M_0 = minimum modulus, and

M = modulus at time 't'.

Substituting torque values for modulus, we get

$$(a - x) = (M_h - M_t) \qquad \text{......} (4)$$

where M_h = the maximum torque developed, and

M_t = the torque at time 't'.

If the reaction is of first order, a plot of ln $(M_h - M_t)$ against 't' should give a straight line whose slope will be the specific reaction rate constant 'k'. Typical plots of ln $(M_h - M_t)$ vs 't' of the blends E_1, E_2 and E_3 are shown in Fig. 1. A straight line graph in each case indicates that the reaction is of first order.

To find out the activation energy of the vulcanization reaction, the modified Arrhenius equation is used

$$t_{90} = A\, e^{E/RT} \qquad \text{......} (5)$$

$$\log t_{90} = \log A + \frac{E}{2.303\, RT} \qquad \text{......} (6)$$

where E = activation energy

t_{90} = time in minutes to attain 90% of maximum torque, and

T = absolute temperature, °K

A plot of log t_{90} vs $1/T$ gives a straight line, from the slope of which E is calculated. Typical plots of log t_{90} vs $1/T$ for the blends E_1, E_2 and E_3 are shown in Fig. 2.

Kinetic factors and cure characteristics

The activation energy E, the first order specific rate constant k and optimum cure time (t_{90}) of the blends at 160°C are given in Table 2. For all the three types of cure systems studied, the activation energy for vulcanization increased and the first order rate constant decreased with increase in the proportion of EVA in the blend. The higher E and lower k values for the compounds J_2 and J_3 compared with those of compounds A_3 and A_3 are due to the fact that EVA has a saturated backbone structure and is less reactive than NR. The increase in E and decrease in k of the sulphur cured blends with over 30 per cent EVA is expected, as EVA cannot be vulcanized by sulphur and the sulphur which is dispersed in the EVA

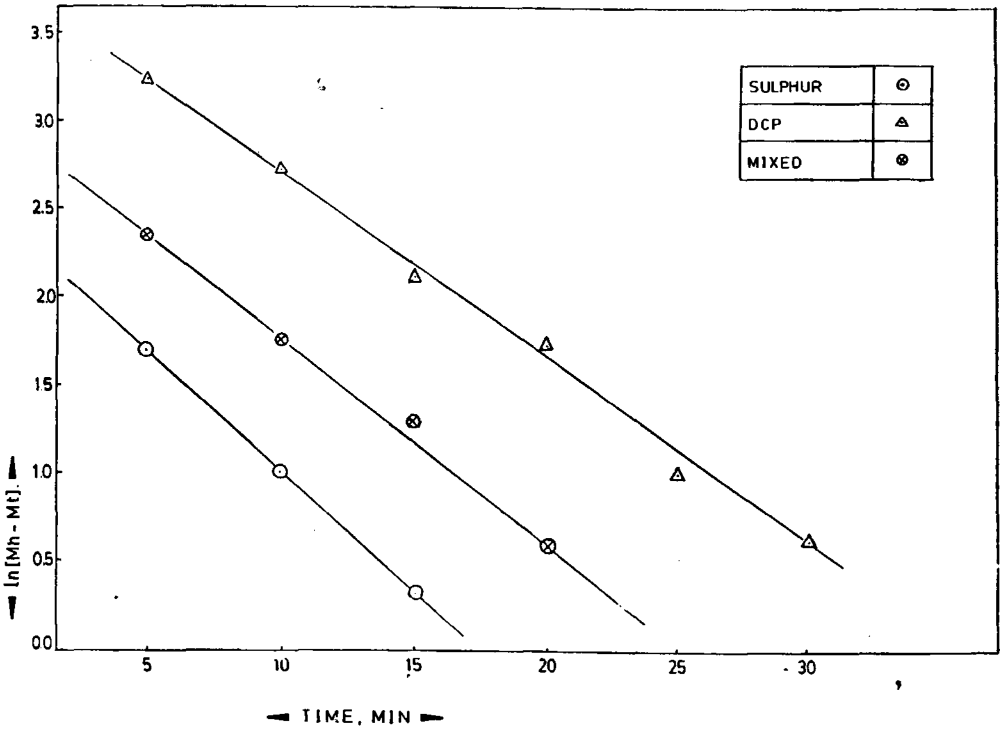

Fig. 1. Plots of ln (M_h - M_t) vs t for blends E_1, E_2 and E_3

phase migrates to the NR phase as the reaction progresses. Between DCP and the mixed cure system, the latter showed lower E and higher k values. While the differences in E were prominent in blends having higher proportions of EVA, the differences between the k values were more evident in blends containing higher proportions of NR. Sulphur is known to act as a co-agent in peroxide vulcanization of elastomers. It is also possible that most of the sulphur remained in the NR phase because of its higher solubility (Van Amerongen, 1964). The higher k values of the mixed cure system compared with those of the DCP cure system can be due to these reasons. These observations are further supported by the optimum cure time of the blends at 160°C. The effect of sulphur in activating peroxide is evident from the lower cure time of the pure EVA compound having the mixed cure system (J_3) compared with that of the DCP cured compound (J_2). While the change in cure time with increase in the proportion of EVA in the blend was only marginal in the DCP cured blends, it was quite significant in the case of blends which contained sulphur and the mixed cure system. The mixed cure system has shorter cure time at all blend ratios of NR and EVA compared with the DCP cure system. Moreover, the cure times of the blends having the mixed cure system were more similar to those of the blends containing the sulphur system, especially at higher proportions of NR in the blends.

Physical properties

Tensile strength, modulus and elongation

The changes in tensile strength, 300%

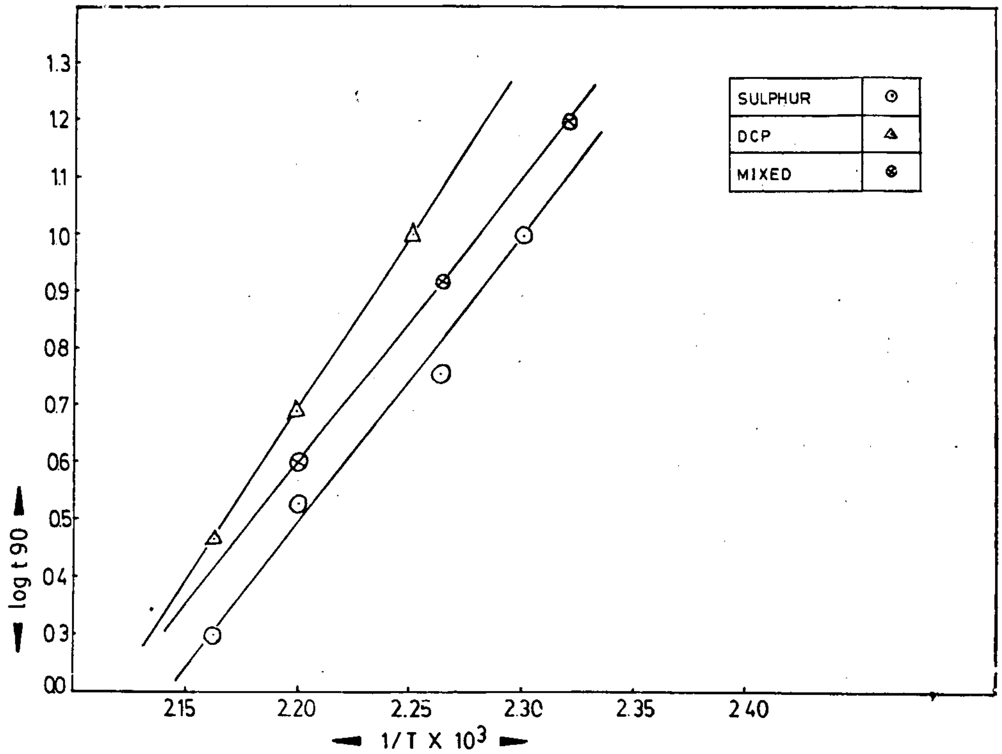

Fig. 2. Arrhenius plots for blends E_1, E_2 and E_3

modulus and elongation at break with increase in EVA content in the blend and the effect of the three different cure systems on these properties are shown in Figs. 3, 4 and 5, respectively. Tensile strength of those blends which contained sulphur and mixed cure systems was maximum when the proportion of NR in the blend was in the range of 70 to 80 per cent, whereas the tensile strength of the DCP cured blends increased steadily with increase in EVA content in the blend. When the proportion of the minor component in the blend is in the range of 20 to 30 per cent, it remains as dispersed particles and the bulk of the curative gets dispersed in the continuous phase. In the present case, this is more pronounced because sulphur is highly reactive with NR and not at all effective in curing EVA. This will facilitate migration of sulphur which is dispersed in the EVA phase to the NR phase during vulcanization. Thus a higher extent of crosslinking of the NR phase of the blends B to D may be the reason for the observed higher tensile values of these blends in the case of sulphur and mixed cure systems.

At higher proportions of NR in the blend, the tensile strength values were in the order: sulphur cure > mixed cure > DCP cure. This observation can be explained based on the type of crosslinks normally obtained when such systems are used. In sulphur cure with conventional dosage, the crosslinks formed are mainly polysulphidic in nature whereas, DCP cure gives carbon-carbon type crosslinks. The more flexible polysulphidic linkages facilitate higher extensions and higher tensile strength during stretching by reforming the ruptured crosslinks in preferred configurations whereas the less flexible C–C type linkages provide only lower tensile strength (Bristow and Tiller, 1970). In the case of the mixed cure system there is a possibility that both the types of crosslinks are formed and the blends attain a higher crosslink density compared to the other cure systems. When mixed crosslinks are present, the tensile strength will be lower because of the unequal distribution of load during stretching (Harwood, 1985). This explains the lower tensile strength of the blends cured with the mixed cure system compared with that of the sulphur cured blends. The higher flexibility of the polysulphidic linkages is also evident from the higher elongation at break of the blends cured with the sulphur and the mixed systems compared with those containing DCP (Fig. 5).

In the case of blends such as those of NR and EVA, crosslink density measurement by the normal swelling method is very difficult because of the wide difference in solubilities and polymer-solvent interaction parameters of the components. However, indirect evidence of a higher crosslink density can be obtained from the modulus values. Figure 4 shows higher modulus values for those blends cured with the mixed cure system compared with those of the sulphur and DCP cured blends at higher proportions of NR. This observation is further supported by the higher rebound resilience values of the blends having mixed cure system (Fig. 6) compared with those of the blends having the other two cure systems. For blends having a higher proportion of EVA also, the mixed cure system gave higher tensile strength than DCP and comparable modulus and resilience values.

Hardness

Hardness of the blends having the different cure systems is shown in Fig. 7. Hardness increased with increase in the proportion of

Table 2. **Activation energy, rate constant and cure time of NR–EVA blends**

Blend Number	Blend ratio NR:EVA	Activation Energy, E (kcal mol^{-1})			Reaction rate constant k			Cure time, t_{90} at 160°C (min)		
		Sulphur	DCP	Mixed	Sulphur	DCP	Mixed	Sulphur	DCP	Mixed
A	100 : 0	15.68	19.44	19.44	0.454	0.117	0.191	7.5	25.5	8.0
B	90 : 10	15.25	20.59	19.44	0.454	0.108	0.207	8.0	24.5	8.5
C	80 : 20	15.23	20.50	20.02	0.454	0.108	0.196	8.5	22.5	10.0
D	70 : 30	15.44	20.31	20.36	0.413	0.107	0.163	9.5	21.5	11.0
E	60 : 40	15.78	21.73	21.34	0.399	0.107	0.140	10.5	22.5	14.5
F	50 : 50	16.01	23.79	21.23	0.374	0.102	0.139	12.5	22.5	16.5
G	40 : 60	16.83	24.39	21.59	0.359	0.105	0.137	13.0	23.0	17.0
H	30 : 70	16.73	24.60	22.08	0.357	0.104	0.130	13.5	22.5	16.5
I	20 : 80	—	24.11	22.28	—	0.100	0.129	—	23.5	17.0
J	0 : 100	—	24.25	22.33	—	0.100	0.126	—	27.5	21.5

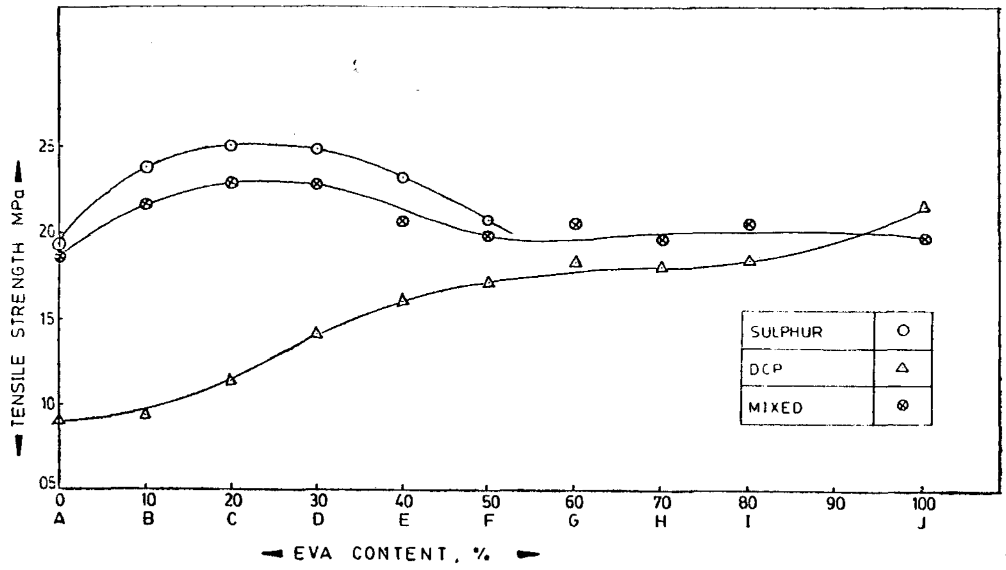

Fig. 3. Effect of blend ratio and cure system on tensile strength

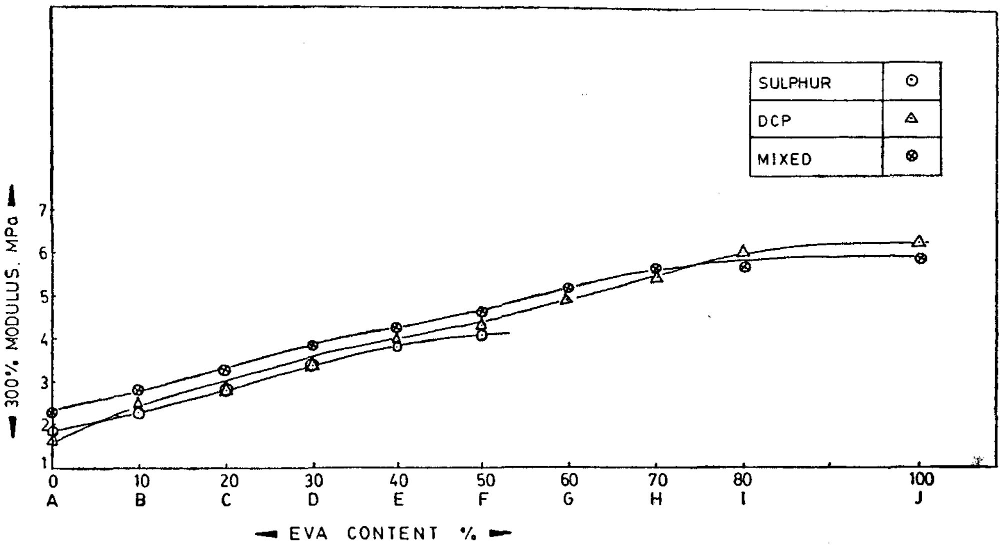

Fig. 4. Effect of blend ratio and cure system on 300% modulus

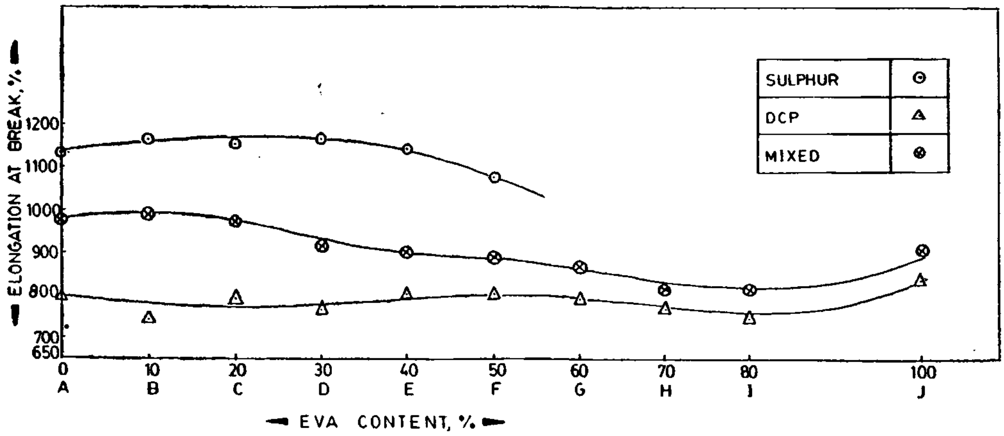

Fig. 5. Effect of blend ratio and cure system on elongation at break

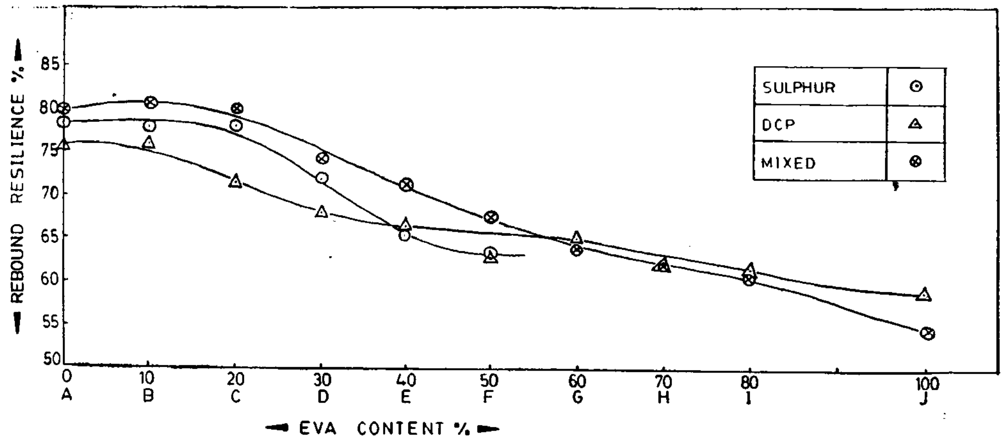

Fig. 6. Effect of blend ratio and cure system on rebound resilience

EVA in the blend. The change in hardness is more sharp in blends E and F compared with the other blends. This is because in these blends EVA also tends to form a continuous phase since its melt viscosity is much lower than that of NR. In hardness measurement, the deformation involved is only at the surface and EVA can form an outer layer during processing. This is the reason for the more or less similar hardness of the blends from F to J. The mixed cure system gave higher hardness in the case of the blends having higher proportions of NR, because of higher extent of crosslinking.

Compression set

Compression set of the blends is found to increase as the proportion of EVA in the blend increased (Fig. 8) which is due to the thermoplastic nature of EVA. For blends A to G the sulphur cure system caused higher set compared with the other two, because of the predominance of polysulphidic crosslinks and also due to the presence of the uncrosslinked EVA phase. It is expected that at the level of 40 per cent EVA in the blend, it can also form a continuous phase because of its lower melt viscosity. Between mixed

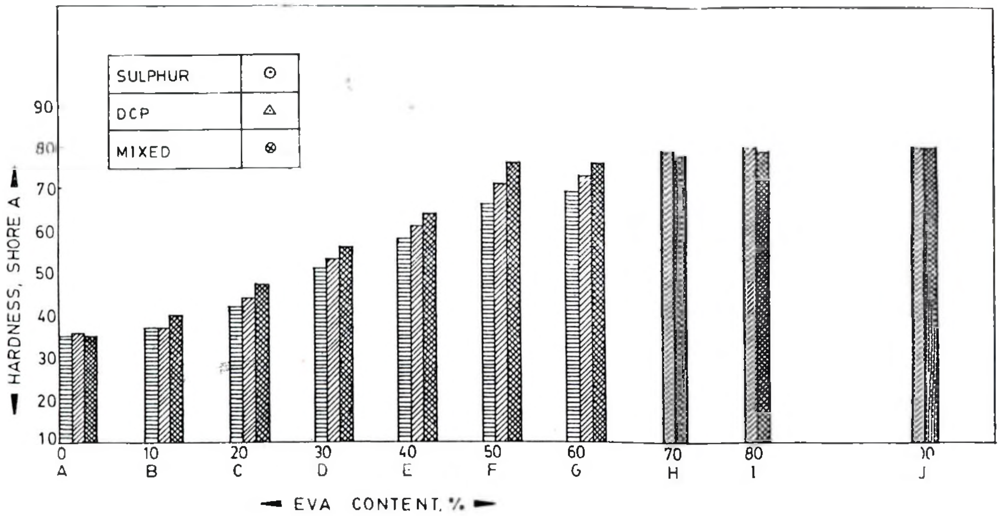

Fig. 7. Effect of blend ratio and cure system on hardness

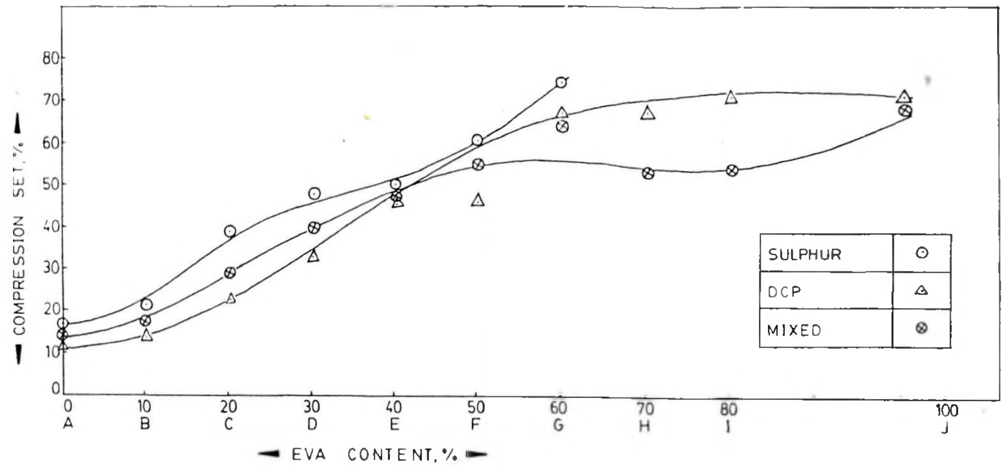

Fig. 8. Effect of blend ratio and cure system on compression set

and DCP cured blends, a change in the compression set pattern was observed at 60:40 NR:EVA (blend E). The mixed cure system which caused higher compression set for blends A to E, showed lower set for blends G to J compared with the DCP cured blends. Blends A_3 to E_3 contained polysulphidic as well as carbon-carbon type crosslinks and hence showed higher set values compared with blends A_2 to E_2 which contained only C–C crosslinks. In blends G to J, NR remained as the dispersed phase. It is possible that the continuous EVA phase of the blends G_3 to J_3 attained higher levels of crosslinking than blends G_2 to J_2 as it is well known that in peroxide vulcanization of EPDM and EVA, sulphur can activate the reaction to produce higher extents of crosslinking (Hofmann, 1967). The dispersed NR phase also can have a higher extent of crosslinking

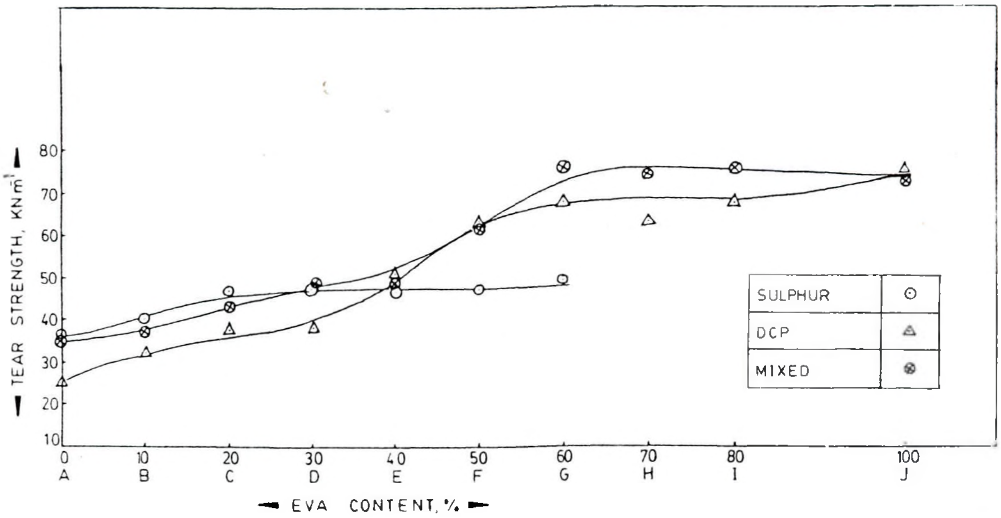

Fig. 9. Effect of blend ratio and cure system on tear strength

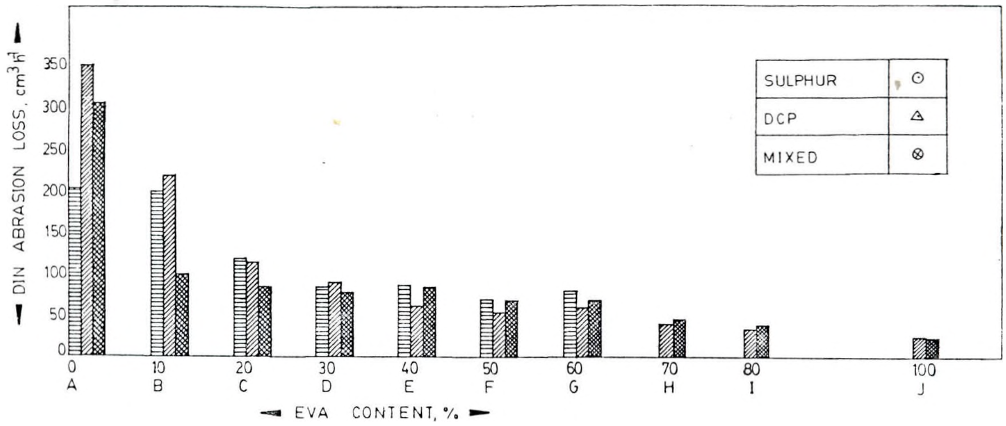

Fig. 10. Effect of blend ratio and cure system on abrasion loss

due to higher solubility of sulphur in this rubber.

Tear and abrasion resistance

Tear resistance of the blends followed similar trend as that of tensile strength (Fig. 9). As the proportion of EVA increased, the tear resistance also increased for the blends with DCP and mixed cure systems. The mixed cure system showed better tear strength compared with DCP cure system at almost all blend ratios. In the case of abrasion resistance also, as the proportion of EVA increased, the blends showed better resistance to abrasion (Fig. 10). The behaviour of the mixed cure system was different in blends having higher proportions of NR and EVA. When the proportion of NR was higher (blends A to D) this system caused better resistance to abrasion than the DCP cure system. However this trend was reversed in blends E to J, in which the DCP cure system gave better abrasion resistance. A similar trend was seen in compression set which was already explained on the basis of the type of crosslinks and extent of crosslinking attained by using the mixed cure system.

CONCLUSIONS

The following conclusions emerge from the present investigations:

1. EVA increases tear resistance, modulus, hardness and abrasion resistance of natural rubber and adversely affects compression set and rebound resilience at all proportions of the two polymers.
2. A mixed cure system consisting of DCP and sulphur gives better technological properties in NR–EVA blends compared with DCP alone, especially at higher proportions of NR in the blend.
3. At higher proportions of EVA, DCP cure gives better abrasion resistance compared to the mixed cure system.
4. Activation energy and cure time of the NR–EVA blends which contained a mixed cure system are much lower than those containing DCP alone.

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