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EFFECT OF BLEND RATIO AND CROSSLINKING SYSTEM ON THE ENGINEERING PROPERTIES OF NATURAL RUBBER - ETHYLENEVINYL ACETATE COPOLYMER BLENDS

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Abstract: Blends of Natural rubber (NR) and ethylene-vinyl acetate (EVA), in varying proportions, were prepared with three different cure systems and evaluated for physical properties. 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.

1. Introduction

A large number of polymer blends have been developed during the course of the past five years in different branches of industry. At or below room temperature, elastomer blends remain in seperate phases, of which 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. It is common practice to prepare and use of blends of two or three elastomers so as to achieve desired processing characteristics and physical properties. Blends of NR and EVA are being used for many applications, such as footwear, cables, etc. A systematic study on the influence of different cure systems and blend ratio on the engineering properties of NR-EVA blends is lacking. In this paper the influence of different crosslinking systems with a view to suggest a cure system suitable for particular blend ratio which has the desired physical properties.

2.Experiment

Materials used

NR used for the study was ISNR_5 and the EVA employed Exxon 218 having vinyl acetate content 18% by weight. All ingredients are of commercial grade.

Preparation of blends

The blends are prepared in a laboratory model intermix set at a temperature of 80 °C and a rator speed of 60 rpm. NR was masticated for 2.0 min and blended with EVA for 2.5 min. The blends were compounded in a two roll mixing mill as per the test recipe in Table 1. Compounds which contained sulpher cure system were designed A1, B1, C1... and those of DCP as A2, B2, C2 .....etc.

Compounds which contained mixed cure system consisting of S and DCP as A3, B3, C3 ..... The blends were moulded to optimum cure in a steam heated hydraulic press at 160°C. Blends with 50% or more of EVA could not be vulcanised fully with sulpher, and hence could not be evaluated for physical properties. The physical properties are evaluated according to ASTM standards.

3. Results and Discussions

Tensile strength, modulus and elongation

The changes in tensile strength, 300% 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. 1,2 and 3 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 percent, 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 sulpher 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[1]. In the case of the mixed cure system there is a possibility that both the types of corsslinks 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[2]. 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. 3).

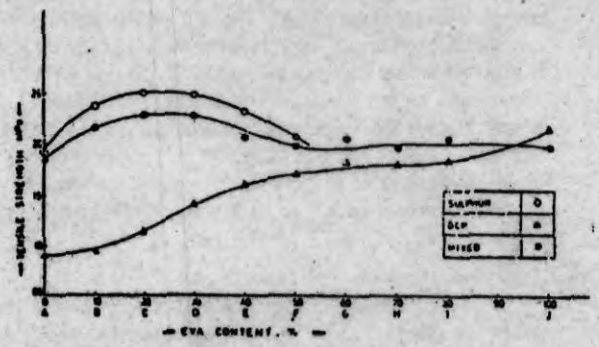

Fig 1.Effect of blend ratio and cure system on tensile strength

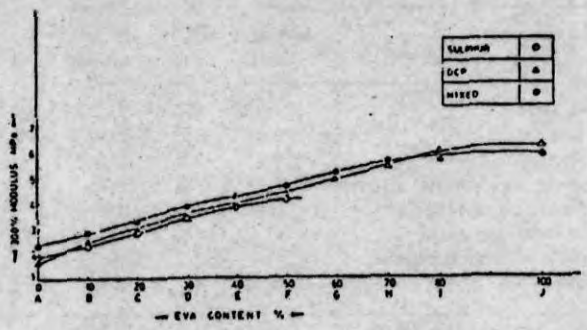

Fig 2.Effect of blend ratio and cure system on 300% modulus

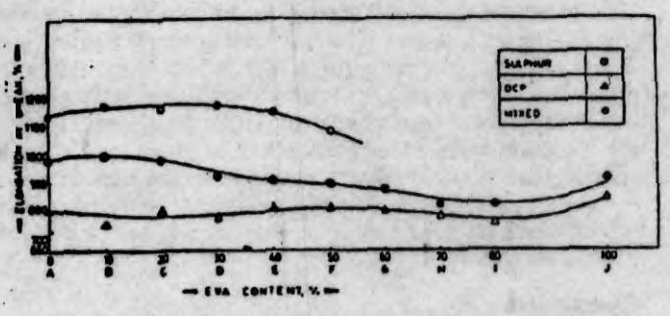

Fig 3.Effect of blend ratio and cure system on elongation at break

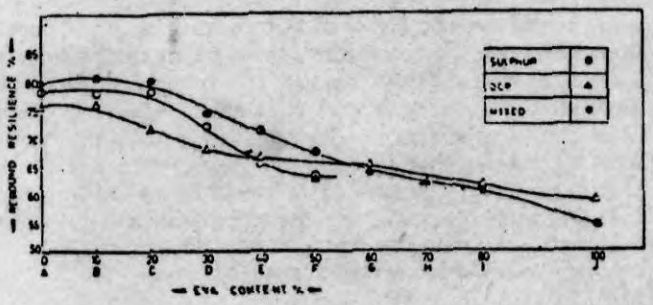

Fig 4.Effect of blend ratio and cure system on rebound resilience

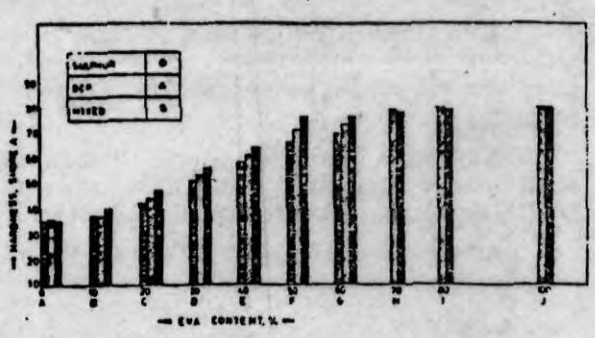

Fig 5.Effect of blend ratio and cure system on hardness

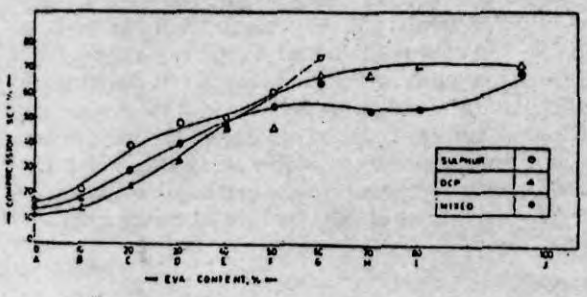

Fig 6.Effect of blend ratio and cure system on compression set

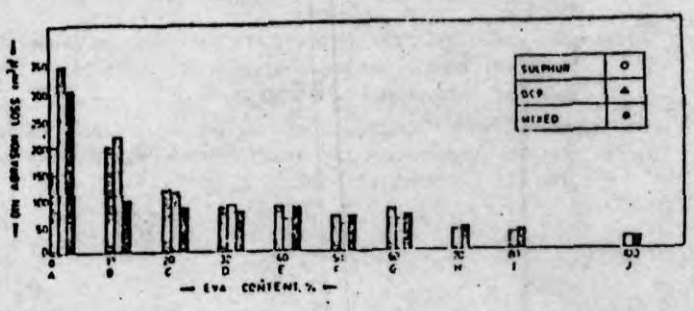

Fig 7.Effect of blend ratio and cure system on abrasion loss

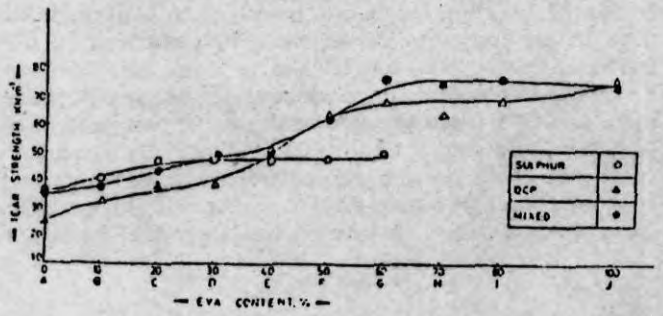

Fig 8.Effect of blend ratio and cure system on tear strength

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
Dibenzothiayl disulphide	0.8	-	0.8
Dicumyl peroxide (40% active ingredient)	-	4.0	4.0
Sulphur	2.5	-	2.5

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 2 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. 4) 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.5. Hardness increased with increase in the proportion of 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. 6) 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 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 A3 to E3 contained polysulphidic as well as carbon-carbon type crosslinks and hence showed higher set values compared with blends A2 to E2 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 G3 to J3 attained higher levels of crosslinking than blends G2 to J2 as it is well known that in peroxide vulcanization of EPDM and EVA, sulphur can activate the reaction to produce higher extents of crosslinking 3. The dispersed NR phase also can have a higher extent of crosslinking 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. 7). 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.8). 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 better abrasion resistance compared to the mixed cure system.

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