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Effect of Blending Techniques on the Curing of Elastomer Blends

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SUMMARY:

Compounding of styrene-butadiene copolymer/polybutadiene, natural rubber/ethylene-propylene-diene terpolymer and natural rubber/butadiene-acrylonitrile copolymer blends was done in three different ways and their curing behaviour and the tensile properties of the vulcanizates are compared.

ZUSAMMENFASSUNG:

Mischungen aus Poly(styrol-co-butadien)/Polybutadien, Naturkautschuk/Poly(ethylen-co-propylen-co-dien und Naturkautschuk/Poly(butadien-co-acrylnitril) wurden nach drei unterschiedlichen Verfahren compoundingiert und Härungsverhalten sowie Zugfestigkeit und Bruchdehnung der Vulkanisate wurden verglichen.

Introduction

Blending of two or more rubbers is carried out for three main reasons¹: 1) improvement in technical properties, 2) better processing and 3) lower compound cost. Many products in the rubber industry are based on blends in all or part of their construction. Tyres are typical examples of products in large scale volume production.

The behaviour of blended rubbers in products cannot simply be considered in terms of rubber/rubber pairs. It depends on many factors such as compatibility of the rubbers, morphology of the phases, dispersion of curatives and fillers in the rubbers, curing aspects etc.²⁻⁶. An attempt has been made to study the influence of different blending techniques on the curing behaviour and the vulcanizate properties of three binary elastomer blends. The results are reported.

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The rubber blends selected for the study were^{7,8}

- A. a compatible blend from non-polar constituents with similar unsaturation (styrene-butadiene copolymer (SBR)/polybutadiene (BR)).
- B. an incompatible blend from non-polar constituents with large difference in unsaturation (natural rubber (NR)/ethylene-propylene terpolymer (EPDM)).
- C. an incompatible blend with similar unsaturation but large difference in polarity (natural rubber (NR)/butadiene-acrylonitrile copolymer (NBR)).

Only gum compounds of 50/50 blends of the above combinations were selected to keep away the effect of filler distribution in the two rubbers.

Experimental

The formulations selected for the individual rubbers are shown in Tab. 1. The formulations were selected such that if the curatives got distributed in the two rubbers according to them, optimum cure could occur in the two constituents of the rubber

Tab. 1. Formulations for individual rubbers.

	NR ^a	SBR ^b	BR ^c	NBR ^d	EPDM ^e
Rubber	100	100	100	100	100
ZnO	5	5	5	5	5
Stearic acid	2	2	2	2	2
CBS ^f	0.6	1.0	0.8	1.5	2.5
TMTD ^g	—	0.8	0.2	0.8	3.0
S	2.5	2.25	2.4	1.5	1.5

^a $M_w = 7.70 \cdot 10^5$; Mooney viscosity, ML (1 + 4) at 100°C 85.3; ISNR 5 (Rubber Research Institute of India).

^b 23.5% styrene; Mooney viscosity, ML (1 + 4) at 100°C 49.2.

^c 97% 1,4-cis; Mooney viscosity, ML (1 + 4) at 100°C 48.0.

^d 33% acrylonitrile; Mooney viscosity, ML (1 + 4) at 100°C 40.9.

^e 3% diene; Mooney viscosity, ML (1 + 4) at 100°C 55.5.

^f N-cyclohexyl benzothiazyl sulphenamides (Indian Explosives Ltd., Rishra).

^g Tetramethyl thiuram disulphide (Indian Explosives Ltd., Rishra).

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blends at about the same time. For each of the rubber blends, SBR/BR, NR/EPDM, and NR/NBR the following blending techniques were employed:

- Type 1. The rubbers were blended together. The total amount of the additives for both the rubbers was then added to the rubber blend.
- Type 2. The compound for each constituent of the blend was prepared separately. Then these compounds were blended together.
- Type 3. The total amount of the additives was added to the slower curing rubber (SBR, EPDM, or NBR). Then the other rubber was blended with this compound.

The compounds were prepared on a laboratory mixing mill according to ASTM D3182 (1982). The cure curves of the various compounds were taken on a Goettfert elastograph model 67.85. The compounds were then vulcanized up to their respective optimum cure times on an electrically heated laboratory hydraulic press. Dumbbell samples for tensile tests were punched out along the mill grain direction from the vulcanized sheets of $15 \times 15 \times 0.2$ cm size. Tensile properties of the vulcanizates were determined at 25 °C as per ASTM D412-80 test method on a Zwick universal testing machine model 1445 at a crosshead speed of 500 mm/minute.

Results and Discussion

Curing Behaviour of the Blends

Fig. 1 shows the curing behaviour of SBR and BR and Fig. 2 shows the curing behaviour of the blends of SBR and BR. All the three types of blends show a combined behaviour of SBR and BR. This may be because the curatives are well distributed between the rubbers without much tendency to preferentially migrate to one of them. This may be due to the compatibility, non-polar nature and fairly equal unsaturations of the two rubbers and hence comparable solubilities of the curatives in them⁹. The last phase of the curing is, however, similar to that of BR, arriving at almost constant torque even before the time noted for BR alone. This might indicate that there is a slight tendency for the curatives to migrate to the BR obviously due to the larger unsaturation¹⁰. This preferential migration might leave BR slightly over-crosslinked and SBR slightly under-crosslinked compared to the individual rubbers.

Fig. 3 shows the cure curves of NR and EPDM and Fig. 4 shows the cure curves of their blends. All the three types of blends exhibit predominantly the behaviour of NR alone. This suggests that the NR phase takes a larger

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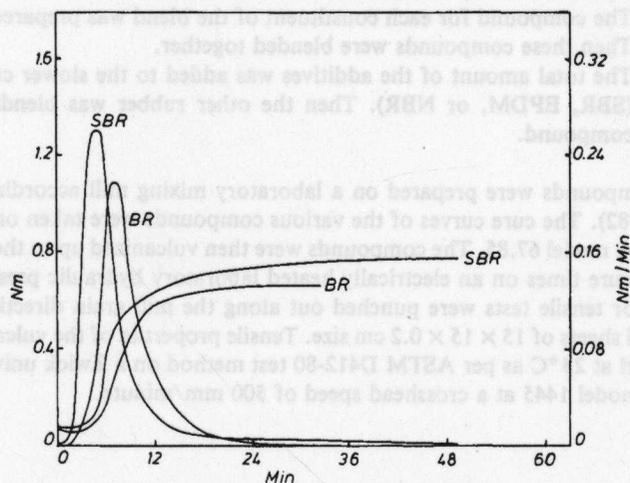


Fig. 1. Cure curves and cure rate curves of SBR and BR.

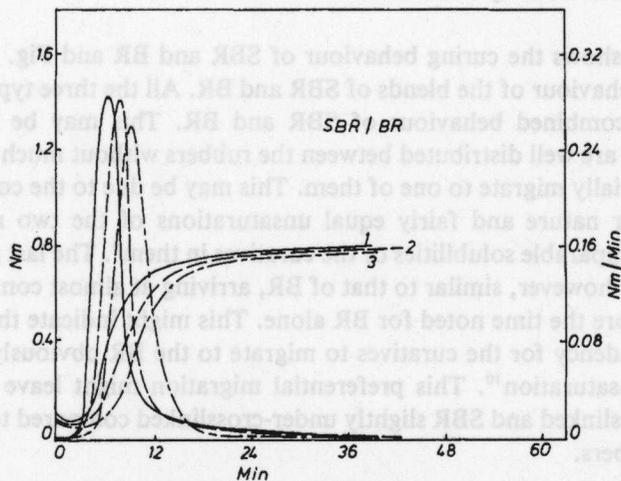


Fig. 2. Cure curves and cure rate curves of SBR/BR blends (1, 2, 3 = blending technique).

share of the curatives due to preferential migration. This preferential migration to the NR phase might have resulted due to the incompatibility of the rubbers and larger unsaturation of the NR phase¹⁰ which results in higher

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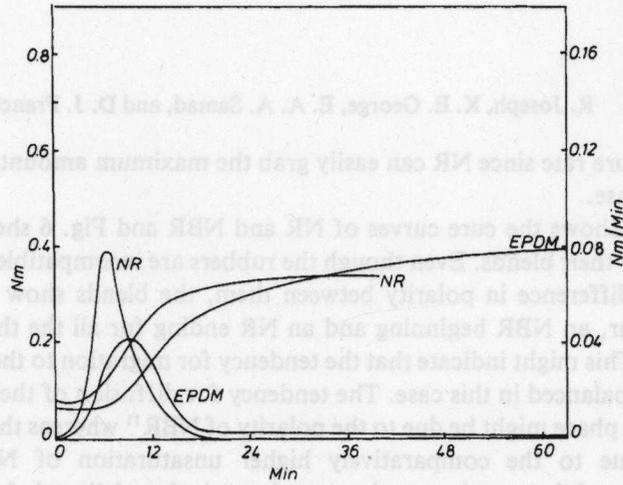


Fig. 3. Cure curves and cure rate curves of NR and EPDM.

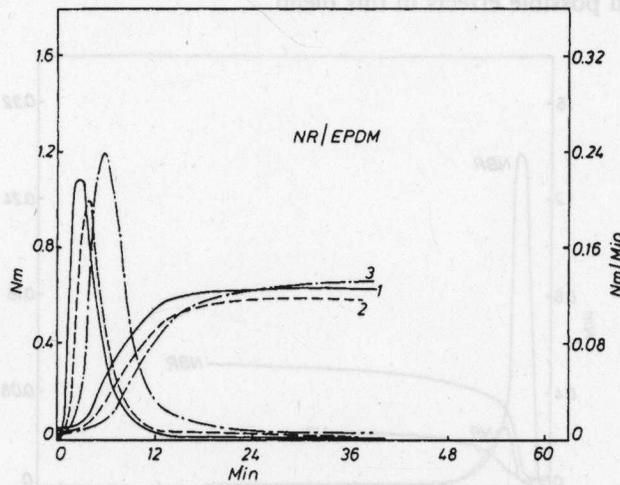


Fig. 4. Cure curves and cure rate curves of NR/EPDM blends (1, 2, 3 = blending technique).

solubilities of the curatives. The EPDM phase which is deprived of its share of curatives might be undercured. As expected the type 1 blend shows the

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fastest cure rate since NR can easily grab the maximum amount of curatives in this case.

Fig. 5 shows the cure curves of NR and NBR and Fig. 6 shows the cure curves of their blends. Even though the rubbers are incompatible and there is a large difference in polarity between them, the blends show a combined behaviour, an NBR beginning and an NR ending for all the three types of blends. This might indicate that the tendency for migration to the two phases is fairly balanced in this case. The tendency for diffusion of the curatives to the NBR phase might be due to the polarity of NBR¹¹ whereas that to the NR phase due to the comparatively higher unsaturation of NR¹⁰. If the migration of the curatives to the two phases is thus delicately balanced, the different blending techniques can shift the distribution of the curatives in the two phases and hence the blending techniques are likely to produce the maximum possible effects in this blend.

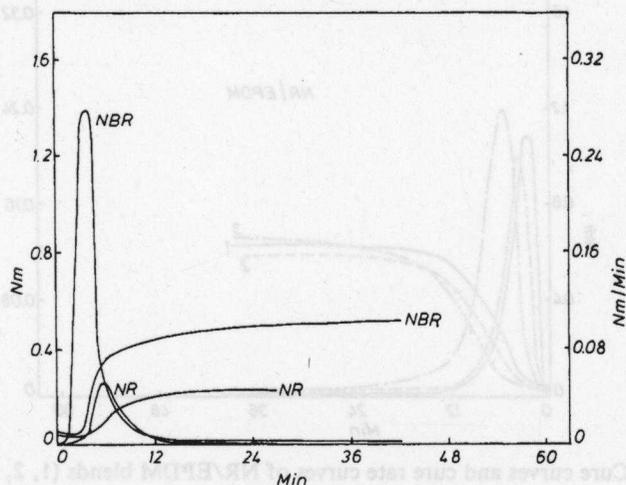


Fig. 5. Cure curves and cure rate curves of NR and NBR.

Tensile Properties

The tensile strength and elongation at break of the rubbers and rubber blends are shown in Tab. 2. The SBR/BR blend might be forming a single phase particularly after the vulcanization¹². The tensile strengths of the blends are close to the additive value of the blend as expected of a

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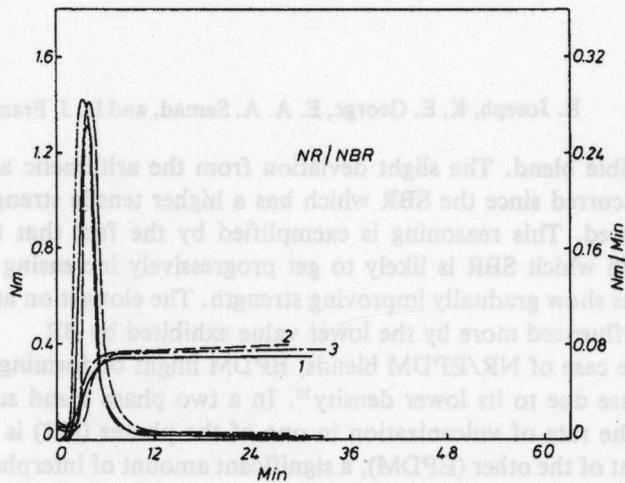


Fig. 6. Cure curves and cure rate curves of NR/NBR blends (1, 2, 3 = blending technique).

Tab. 2. Tensile properties of the vulcanizates.

Rubber/Rubber blend	Tensile strength (MPa)	Elongation at break (%)
SBR	2.20	200
BR	1.50	150
SBR/BR 1	1.68	140
SBR/BR 2	1.75	145
SBR/BR 3	1.82	150
NR	16.00	700
EPDM	1.50	150
NR/EPDM 1	3.02	168
NR/EPDM 2	2.81	162
NR/EPDM 3	2.56	156
NR	16.00	700
NBR	1.50	150
NR/NBR 1	12.1	653
NR/NBR 2	11.0	673
NR/NBR 3	10.0	693

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compatible blend. The slight deviation from the arithmetic average might have occurred since the SBR which has a higher tensile strength is slightly undercured. This reasoning is exemplified by the fact that type 2 and 3 blends in which SBR is likely to get progressively increasing share of the curatives show gradually improving strength. The elongation at break seems to be influenced more by the lower value exhibited by BR.

In the case of NR/EPDM blends, EPDM might be forming the continuous phase due to its lower density¹⁰. In a two phase blend such as this in which the rate of vulcanization in one of the phases (NR) is much higher than that of the other (EPDM), a significant amount of interphase crosslinking also might be absent¹. Hence the tensile properties are more likely to be affected by the EPDM phase and this might be the reason for the low value of the strength. The improvement in tensile strength over that of EPDM is only little and this seems to be largely influenced by the degree of crosslinking in the NR phase. The elongation at break is also similar to that of the EPDM rubber, which forms the continuous phase.

In the case of the NR/NBR blends, the tensile strengths observed are higher than the arithmetic average of the constituents even though they are also likely to form two-phase blends. The high values of strength suggest that the NR forms the continuous phase or that both phases exist in the continuous state. Also, the rate of vulcanization in the two phases might be comparable which permits the formation of a significant amount of interphase crosslinks. The actual value of the strength seems to be affected more by the degree of crosslinking in the NR phase, which has higher strength, as expected. The amount of curatives in the NR phase might be the maximum in blend 1 which shows the maximum strength and least in blend 3 which shows the least strength. The elongation at break is again found to be more influenced by the continuous phase.

Conclusions

The following conclusions could be drawn about the curing behaviour and vulcanize properties of elastomer blends:

1. The distribution of curing agents largely depends on the nature of the rubbers. The curing agents tend to migrate preferentially to the rubber with higher unsaturation or higher polarity.
2. If for a given rubber blend the tendency of the curatives for migration into the two rubbers is nearly the same, the blending parameters can

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influence to a great extent the distribution of the curatives in the two rubbers and hence the mechanical properties of the blend.

3. The mechanical properties of the vulcanizates of elastomer blends seem to be most affected by the degree of crosslinking in the two rubbers and the rubber which forms the continuous phase.

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