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CURE CHARACTERISTICS AND MECHANICAL PROPERTIES OF CARBON BLACK FILLED STYRENE–BUTADIENE RUBBER AND EPOXIDIZED NATURAL RUBBER BLENDS

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Abstract—Carbon black filled styrene–butadiene rubber (SBR) and epoxidized natural rubber (ENR) blends were cured, mainly using the efficient vulcanization system (EV). The effects of mixing method, blend ratio, loading and type of carbon black and two other vulcanization systems on cure characteristics and mechanical properties were examined. The masterbatch technique of mixing gives rise to more consistent cure characteristics and mechanical properties. The results clearly indicate that ENR behaves more like SBR than natural rubber (NR). As expected, the properties, particularly the mechanical properties, are strongly influenced by blend ratio, loading and type of black, and the vulcanization system.

INTRODUCTION

Polymer blends are being used extensively in numerous applications; this statement is also true with rubber blends, especially in tyre manufacture. Apart from blends of common rubbers, speciality rubber are also being utilized, depending on service demands and components of the tyre [1, 2]. Many reports covering a wide range of rubber blends have been published [3–6]. The use of carbon black is synonymous with the history of tyres. Although it has lost some ground to other reinforcing fillers such as silicas, by virtue of its unrivalled performance, it is still the most popular and widely used reinforcing filler. However, the primary properties of carbon blacks are normally controlled by particle size, surface area, structure and surface activity and they are in most cases interrelated [7, 8].

Epoxidized natural rubber (ENR) is a new rubber, having properties resembling those of synthetic rubbers rather than natural rubber (NR) [9, 10]. It can offer unique properties such as good oil resistance, low gas permeability, improved wet grip and rolling resistance, coupled with high strength. In this study, the cure characteristics and mechanical properties of carbon black filled blends of ENR and styrene–butadiene rubber (SBR) were investigated. The effects of mixing method, blend ratio, content and type of carbon black, and vulcanization system are compared and presented.

EXPERIMENTAL

Materials and formulations

ENR 50 was supplied by the Rubber Research Institute of Malaysia (RRIM) while SBR 1502 and other ingredients [viz. sulphur, zinc oxide, stearic acid, process oil, tetramethylthiuram disulphide (TMTD), *N*-cyclohexylbenzothiazole-2-sulphenamide (CBS) and *N'*-phenyl-*p*-phenylene diamine (IPPD)] were obtained from local rubber chemical suppliers. Four grades of carbon black, viz. HAF (N330), FEF (N550), GPF (N660) and SRF (N774), were purchased from Malaysian Carbon (M) Ltd.

The full recipes are shown in Table 1. To enable optimum conditions to be selected, the effect of mixing was first studied.

Mixing and measurement of cure characteristics

Mixings were carried out using a laboratory two-roll mill. Two techniques were examined, viz. the masterbatch and the premix techniques. In the first technique, SBR and ENR masterbatches containing carbon black and aromatic oil were separately prepared. Then, both masterbatches were compounded together with the remaining ingredients. In the second technique, SBR and ENR were first premixed, prior to the addition of other ingredients. Both techniques were equally timed at around 16 min. The masterbatch technique was preferred for subsequent experiments.

The cure characteristics of the mixes were determined with a Monsanto rheometer model R. 100 at 150°. The Mooney scorch, t_5 at 120° was also measured, using a Mooney viscometer. The compounds were then com-

Table 1. Formulations of carbon black filled SBR/ENR elastomer blends

Ingredients	pphr
SBR (1502)	0–100
(ENR 50)	100–0
Carbon black[a]	0–80
Process oil[b]	5
Zinc oxide	5
Stearic acid	2
IPPD	2
Sulphur[c]	0.3
CBS[c]	2.4
TMTD[c]	1.6

[a]Content and type of black vary with experiments.
[b]Dutrex 729 (Shell Chem. Co).
[c]Amounts shown are those for the EV system, while for the CV and TMTD systems the following amounts were used: S, 2.5; CBS, 0.6; and TMTD, 2.4.

Table 2. Cure characteristics and mechanical properties of SBR/ENR elastomer blends with 60 pphr N330 carbon black, cured using the EV system at 150°

	0/100	25/75	50/50	75/25	100/0
Mosanto rheometer, 150°[b]					
M_{HP}, torque unit[a]	51.5	55.5 (61.8)	62.0 (74.8)	63.5 (68.5)	62.5
M_L, torque unit	4.5	7.0 (7.8)	9.0 (21.8)	10.0 (21.8)	9.5
Cure time, t_{90} (min)	6.2	6.8 (10.0)	7.0 (7.8)	7.3 (9.0)	8.0
Scorch time, t_2 (min)	4.3	4.3 (3.8)	4.5 (3.8)	4.8 (3.5)	5.0
Mooney scorch, t_5, 120°	14.5	15.5 (15.0)	18.0 (12.5)	14.5 (15.5)	16.0
Mechanical properties[b]					
Modulus at 100% elongation (MPa)	1.3	1.7 (2.5)	1.9 (2.6)	1.6 (2.2)	1.3
Modulus at 300% elongation (MPa)	7.8	8.3 (12.1)	8.3 (14.2)	8.8 (8.5)	8.4
Elongation at break, EB (%)	516	496 (484)	569 (458)	540 (623)	651
Tensile strength, TS (MPa)	18.0	17.0 (16.5)	18.4 (17.3)	19.7 (20.8)	20.9
Tear strength (N/mm)	11.8	14.3 (13.6)	14.0 (12.8)	16.4 (16.8)	19.9
Resilience, Dunlop (%)	24.1	27.0 (25.5)	30.2 (27.0)	35.2 (34.0)	43.9
Hardness, IRHD	56.5	61.1 (67.9)	61.3 (70.4)	62.8 (68.3)	63.5

[a]1 torque unit = 1 in lb = 0.11 Nm.
[b]Values in parentheses are those obtained for premix technique of mixings.

pression moulded at 150° using the respective cure times (t_{90}).

Measurement of the mechanical properties

The tensile properties and tear strength of the vulcanizates were determined using an Instron Universal Testing Machine according to BS 903: Pt A2 (1971) and BS 903: Pt A3 (1972), respectively. Other mechanical properties examined were as follows: hardness (IRHD) was measured using a Wallace dead load tester according to BS 903: Pt A26 (1969) and resilience was obtained using a Wallace Dunlop tripsometer following BS 903: Pt A8 (1963).

RESULTS AND DISCUSSION

Effects of mixing and blend ratio

The cure characteristics and the mechanical properties of filled SBR/ENR, having varying blend ratio and prepared using the two mixing techniques, are shown in Table 2. The values derived from the premix technique are shown in brackets. The efficient vulcanization (EV) system was chosen, rather than other vulcanization systems, because it is in vogue for ENR [9, 10].

Comparing the two techniques, it is evident that clearer consistent trends in both cure characteristics and mechanical properties of SBR/ENR were obtained using the masterbatch technique. Perhaps it can be deduced that this technique produces more consistent and homogenous SBR/ENR blends, although there are instances in which the premix technique gives rise to blends having marginally superior mechanical properties. For example, the 50/50 and 75/25 blends exhibit higher modulus at 300% elongation and tensile strength, respectively.

The better mixing obtained through the masterbatch technique arises because, prior to the final compounding, the two rubber masterbatches were mixed separately. Hence, the chance for uneven sharing of the black by the two rubbers was minimized. As a result, when the two masterbatches were later compounded, better homogeneity and degree of dispersion in the two phases were obtained. However, the situation is different with premix mixing. Here, uneven sharing of the black by the two rubber phases was inevitable, as clearly shown by Hess *et al.* [3]. This normally happens when the two rubbers are immiscible or the blend consists of microdispersions of one in the other.

Working with a blend of NR and polybutadiene (BR), they found that better properties were obtained when BR contained more black. However, with a 50/50 blend, they observed that the black was preferentially incorporated in the NR. A similar situation might have occurred with the premix 50/50 SBR/ENR blend. Here, instead of the SBR, which is the harder of the two rubbers, and also the poorer compatibility of the blend, it is the weaker ENR which has the more black. This perhaps explains why poorer and inconsistent properties were obtained with the premix SBR/ENR blend. However, there are many instances [4, 11] in which this effect might not be so pronounced and where, apart from filler dispersion, the degree of crosslinking has to be considered.

Referring only to the data derived from masterbatch mixing, increasing the SBR results in marginally improved cure characteristics, seen from the cure and scorch times. Furthermore there is an increasing trend in torque, except for the 75/25 blend ratio. Similarly, increasing trends were observed with the vulcanizate properties such as tensile strength, tear strength, resilience and hardness. However, maximum moduli at 100 and 300% elongations, occur at 50/50 and 75/25 blend ratios, respectively, while maximum elongation at break is found at 50/50 blend ratio.

An explanation similar to that given earlier could perhaps be applied here. With increasing SBR and a corresponding reduction in ENR, the time for black uptake in ENR is more rapid. Further, as more SBR is present, there is a consequent drop in the maximum loading capacity of ENR, hence more black uptake can be shared by the SBR. The increased black in SBR therefore explains the marginal improvement in properties. Here, the amount of black to be incorporated is constant throughout. In other words, the depleting ENR forces excess black into the SBR, consequently better sharing of the two rubber phases occurs. However, further studies on the morphological nature of black distribution in SBR/ENR are needed before a conclusion can be drawn.

The properties of ENR which are well-known to be akin to SBR [9, 10], rather than NR, might have also

Table 3. Cure characteristics and mechanical properties of 50/50 SBR/ENR with various amounts of N330 carbon black, cured using the EV system at 150°

	Loading of N330 carbon black, pphr				
	0	20	40	60	80
Monsanto rheometer, 150°					
M_{HP}, torque unit	49.0	55.5	56.6	62.0	78.2
M_L, torque unit	7.0	6.8	7.3	9.0	14.0
Cure time, t_{90} (min)	9.3	7.4	6.9	7.0	12.0
Scorch time, t_2 (min)	6.0	4.3	4.0	4.5	3.8
Mooney scorch, t_5, 120°	28.0	17.5	19.0	18.0	13.5
Mechanical properties					
Modulus at 100% elongation (MPa)	0.7	1.0	1.3	1.9	3.4
Modulus at 300% elongation (MPa)	1.6	4.3	6.5	8.3	16.4
Elongation at break, EB (%)	690	650	706	569	424
Tensile strength, TS (MPa)	2.3	11.7	20.9	18.4	17.9
Tear stength (N/mm^2)	3.9	7.4	11.3	14.0	17.2
Resilience, Dunlop (%)	53.1	42.1	35.6	30.2	23.4
Hardness, IRHD	42.2	49.3	54.5	61.3	76.7

contributed towards enhancing the compatibility between the two rubber phases and the better sharing of black. The presence of epoxide groups in ENR has been found to introduce some degree of polarity, so explaining the increased resistance to hydrocarbon oils, and to improve compatibility with polar polymers such poly (vinyl chloride) [12, 13]. Another interesting point is that marginally poorer mechanical properties than SBR are shown by the blends, with a few exceptions, although ENR is known to undergo strain-induced crystallization when subjected to stress [9, 10].

Effect of loading and type of black

It is common practice to vary the loading and type of carbon black in order to derive optimum reinforcement and also to reduce cost. Table 3 shows the cure characteristics and the mechanical properties of 50/50 SBR/ENR, having various contents of N330 black. As expected, increasing the black increases properties such as torque, moduli at 100 and 300% elongations, tear strength and hardness but at the same time reduces resilience. Elongation at break, however, shows an initial drop, followed by a rise whereas tensile strength shows exactly the opposite pattern with increasing loading. Both inflections occur around 40 pphr loading.

The improvement in most properties with increasing loading might be explained as follows. As mixing progresses, the softer ENR takes up most of the black until its maximum capacity is achieved, after which the SBR shares in the black uptake. With further increase in black, the amount to be shared by SBR increases also. This goes on until the maximum capacity is attained. Beyond this point, a further increase in black results in a drop in properties. If compatibility between ENR and SBR phases is taken into consideration, then there may be a slightly different picture. Here, the rates of black uptake by both rubbers are approximately equal, hence there might be better sharing of black by the rubber phases. The smaller disparity in black dispersion between both phases would ultimately impart improved mechanical properties with increasing loading. Similarly, a drop would occur once the maximum levels are reached.

A less clear pattern was observed with cure characteristics. Here, neither the cure and scorch times nor the Mooney scorch show definite falling or rising trends with increasing loading. The only exception is the maximum torque which rises with increasing loading. Similar observations have been reported by Cotten [8] and Wolff [15] in which a significant increase in maximum torque occurs with increase loading and this rise in torque has been used to evaluate the filler reinforcement. Although, filler reinforcement is controlled by numerous interrelated factors [7, 8], here stress is mainly governed by particle size. The cure characteristics and the mechanical properties of 50/50 SBR/ENR blends filled with 40 pphr black are given in Table 4. The N330 has the smallest size or larger external surface area, followed by N550, N660 and then N774. As expected, no significant trend in cure characteristics of the different blacks was observed, although N330 shows marginally faster cure and higher torques but with Mooney scorch comparable to N774. Curing properties of vulcanizates, especially those which are polar in nature like chloroprene or nitrile–butadiene rubbers, can also be strongly affected by the presence of hydroxyl or other oxygen-containing groups on the surface of the carbon black [16].

For mechanical properties, decreasing the particle size generally enhances properties such as moduli at 100 and 300% elongations, tensile strength, tear strength and hardness but decreases the resilience. However, there are exceptions, particularly for N774, which exhibits the highest elongation at break and also greater tensile strength than the N660. This clearly indicates that in some instances other filler characteristics are of paramount importance. However, excluding the few anomalies, one can perhaps explain the improved properties with decreasing particle size in SBR/ENR blends as follows. As the size decreases, assuming all have more or less identical shapes, the void volumes to be filled and the black uptake by ENR also become smaller. Consequently, there would be more void volumes which can be filled by SBR, hence the improved properties observed with reducing size of black. Many studies on the effects of the filler characteristics on vulcanizate properties have been reported [7, 8, 14].

Table 4. Cure characteristics and mechanical properties of 50/50 SBR/ENR elastomer blends having 40 pphr loading of different grades of carbon black, cured with the EV system at 150°

	Grades of carbon black			
	N330	N550	N660	N774
Monsanto rheometer, 150°				
M_{HP}, torque unit	56.6	55.0	55.3	52.3
M_L, torque unit	7.3	6.3	5.8	5.8
Cure time, t_{90} (min)	6.9	7.6	8.3	8.0
Scorch time, t_2 (min)	4.0	4.5	4.5	4.5
Mooney scorch, t_5 (min)	19.0	21.5	20.0	19.0
Mechanical properties				
Modulus at 100% elongation (MPa)	1.3	1.3	1.2	1.0
Modulus at 300% elongation (MPa)	6.5	5.7	5.4	4.5
Elongation at break, EB (%)	706	616	597	735
Tensile strength, TS (MPa)	20.9	11.9	11.2	14.9
Tear strength (N/mm²)	11.3	10.5	9.7	9.5
Resilience, Dunlop (%)	35.6	41.4	43.4	42.6
Hardness, IRHD	54.5	50.8	51.6	49.3

Effect of vulcanization system

It is well-known that various vulcanization systems give rise to dissimilar vulcanizate structures and hence different properties [12, 17]. Here, the effects of EV, CV and sulphur-less TMTD systems on the properties of filled 50/50 SBR/ENR blends were examined and the results are shown in Table 5. As may be seen, the EV system exhibits the fastest cure and the highest Mooney scorch; the CV system imparts the highest maximum torques and slowest cure and scorch times, whereas the TMTD system shows the smallest maximum torque, Mooney scorch and the most rapid scorch time. However, the latter shows comparable minimum torque as the CV system. As for the mechanical properties, the CV system gives rise to overall superior properties (viz. moduli at 100 and 300% elongation, tear strength, resilience and hardness). However, the EV system exhibits marginally higher tensile strength and lower resilience than the CV system, while the TMTD system, interestingly, gives the best elongation at break. Further, it also imparts a higher tear strength than the EV system.

From both properties it is evident that, for SBR/ENR filled blends, each system has its own merits. It is well-known that the CV system, due to its predominantly polysulphidic crosslinks, gives rise to high strength [12, 17], whereas, by virtue of their dominantly mono- and disulphidic crosslinks, the other two systems are associated with poorer mechanical properties. However, this general pattern unfortunately only applies to some rubbers. One obvious exception is ENR. Gelling [18] has reported that for ENR, because of the different crosslinking mechanism, a semi-EV or EV system normally exhibits better performance than CV system. Further with blends and black being present, the choice of vulcanization system would obviously depend on many factors including end uses and service demands. Finally, in all cases studied, phenomena such as reversion or marching cure which are common to both NR and SBR respectively, are completely unobserved. Hence, the blend properties are fairly constant once the maximum cure is attained and obviously the processing is simplified.

CONCLUSIONS

The following conclusions can be drawn on the cure characteristics and vulcanizate properties of filled SBR/ENR blends:

(a) Both the cure characteristics and mechanical properties of SBR/ENR blends clearly show that ENR is more akin to SBR than NR.

Table 5. Effects of different vulcanization systems on the cure characteristics and mechanical properties of 50/50 SBR/ENR elastomer blends containing 40 pphr N330 carbon black

	Vulcanization systems		
	CV	EV	TMTD
Monsanto rheometer, 150°			
M_{HP}, torque unit	62.5	56.5	40.5
M_L, torque unit	7.5	7.3	7.5
Cure time, t_{90} (min)	9.5	6.9	8.3
Scorch time, t_2 (min)	5.3	4.0	3.5
Mooney scorch, t_2 (min)	18.5	19.0	12.0
Mechanical properties			
Modulus at 100% elongation (MPa)	1.6	1.3	0.8
Modulus at 300% elongation (MPa)	8.0	6.5	4.2
Elongation at break, EB (%)	663	706	834
Tensile strength, TS (MPa)	20.7	20.9	18.3
Tear strength (N/mm²)	19.0	11.3	13.3
Resilience, Dunlop (%)	36.8	54.5	49.6
Hardness, IRHD	57.9	54.5	49.6

Hence, more compatible and homogenous filled blends were obtained.

(b) The masterbatch technique of mixing generally produces vulcanizates having more consistent cure characteristics and vulcanizate properties, although there are instances where the premix technique gives better performance.

(c) A clear effect of carbon black loading and type of mechanical properties was observed, for vulcanization systems, each having its own advantages although the CV system exhibits overall superior performance.

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