The Effect of a Diamine Salt of Fatty Acid on Carbon Black Filled NR Compounds Properties Using Random Mixing

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ABSTRACT

The effect of a diamine salt of fatty acid termed a multifunctional additive (MFA) on carbon black filled natural rubber properties using random mixing has been studied. A similar effect of the MFA on mechanical properties is obtained as in sequence mixing. The addition of MFA improves the mechanical properties of carbon black filled natural rubber compounds. However, the improvement of these properties can only be obtained if the amount of this additive used does not exceed the critical level. Above the critical level, a gradual deterioration of properties occurs as a result of a weak interaction at the MFA-MFA interface. These results confirm the previous works using the sequence mixing.

Key Words: carbon black, mechanical properties, natural rubber, random mixing, multifunctional additive

INTRODUCTION

A multifunctional additive (MFA) is a cationic surfactant which has the general formula of $[RNH_2^+(CH_2)_3NH_3^+][R'COO^-]_2$. In our previous reports [1–3], all natural rubber/carbon black mixes filled with different levels of MFA were carried out using a sequence of mixing in which the control compound was mixed first, followed by compounds with increasing levels of MFA.

Compared to the control, the addition of the multifunctional additive has been found to show an enhancement in vulcanizate and dynamic properties up to a level of 2 phr, after which there is a gradual deterioration of these properties.

Carbon black dispersion test measured by computer-aided image analysis of a cut surface and scanning electron microscopy (SEM), showed a substantial improvement with increasing MFA level. The greatest improvement was observed between 0 and 1 phr. It is possible that the poor quality of the control (SEM micrograph) and lower vulcanizate properties, compared with mixes filled with MFA, could be due to mixer start-up

transients (the first batch effect), rather than the quality of the mix affected by MFA. Therefore, in this work the order of mixing has been randomized so that any inefficiency of mixing caused by heat-sink effects would be overcome or eliminated. This is important to show that the changes in mechanical properties are due to MFA concentration and not due to the order of mixing.

EXPERIMENTAL

Materials

The materials used as in ref 1: natural rubber-SMR 20, carbon black-N330, MFA-EN444, from Akzo Ltd.

Procedures

The formulation, mixing cycle and test procedure are similar as in the sequence mixing [1,2]. The order of mixing has been randomized and the mixing sequence used was: 1.0 phr; control; 3.0 phr; 2.0 phr; 5.0 phr; and 0.3 phr.

In this work only SEM was used to measure the carbon black dispersion in all the compounds prepared.

RESULTS AND DISCUSSION

Vulcanizate and Dynamic Properties

Table 1 shows the compound and vulcanizate properties. It can be seen that the compound properties, i.e. scorch time, t_5 and cure time, t_{95} are not much different compared to sequence mixing (Figure 1). The reduction of scorch and cure time with MFA addition is due to the dissociation of MFA into a diamine and fatty acid at temperature higher than 120 °C [3]. Tensile strength, tensile modulus, tear strength, hardness and abrasion resistance also show the similar trend as reported in our previous sequence mixing [1–3].

Figure 2 shows the tensile strength comparison for random and sequence mixing. As in

Table 1. Properties of six SMR 20/N330 mixes filled with different levels of MFA (random mixing).

Properties	MFA(phr)					
	0	0.3	1	2	3	5
Compound Properties[a]						
Max. torque (Nm)	2.54	2.60	2.59	2.60	2.52	2.15
Min. torque (Nm)	0.67	0.67	0.65	0.62	0.62	0.53
Scorch time, t_5 (s)	49	42	29	26	24	18
Curing time, t_{95} (s)	404	375	329	299	283	258
Vulcanizate Properties						
Hardness (IRHD)	68	69	69	70	69	68
Tensile strength (MPa)	25.1	26.0	26.4	26.8	26.6	25.8
Elongation at break(%)	498	458	440	414	448	463
100% Modulus (Mpa)	3.5	3.6	3.8	3.9	3.7	3.6
300% Modulus (MPa)	14.8	16.3	16.5	16.6	16.4	15.3
Tear strength ($kN.m^{-1}$) (trouser)	47	55	62	72	50	49
Tear strength ($kN.m^{-1}$) (crescent)	70	86	98	101	96	94
Abrasion resistance, DIN (vol. loss/mm^3)	74	73	73	71	75	78

[a] Wallace Precision Cure Analyzer at 160 °C.

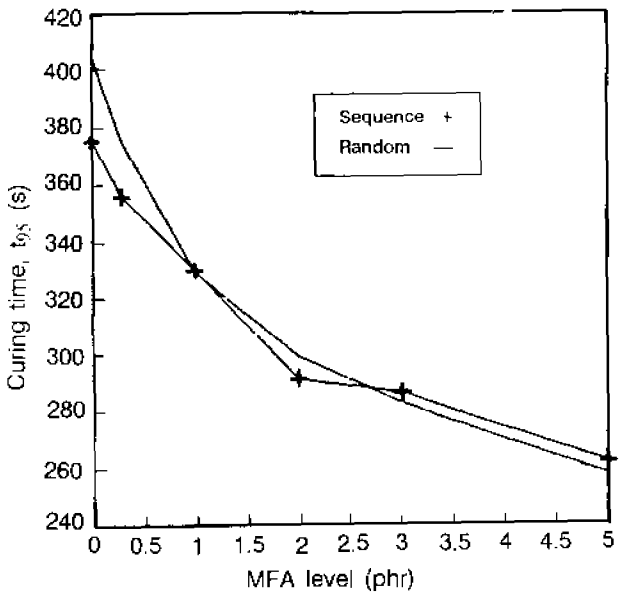


Figure 1. Curing time, t_{95} comparison for sequence and random mixing.

sequence mixing, compared to the control, the addition of MFA from 0.3 to 2 phr has increased tensile strength up to an optimum value, after which gradual deterioration is obtained. A similar effect by MFA can also be seen in tear strength (Figure 3) and modulus 300 (Figure 4).

For dynamic properties, the in-phase shear modulus, G' obtained by random mixing also confirmed the results shown by sequence mixing. The trends are similar as for tensile strength and

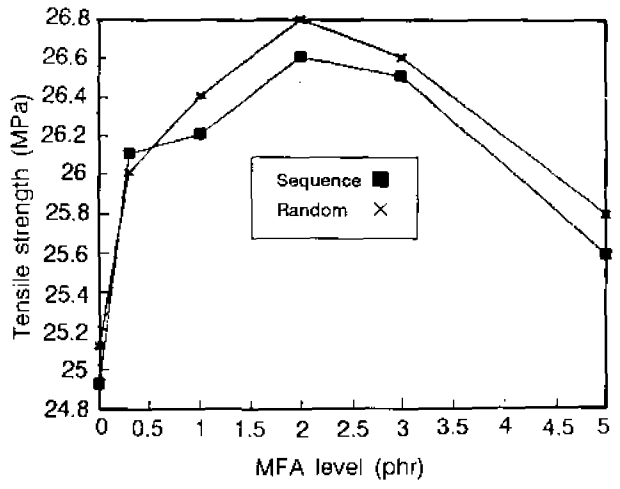


Figure 2. Tensile strength versus MFA level for random and sequence mixing for NR/CB N330 mixes.

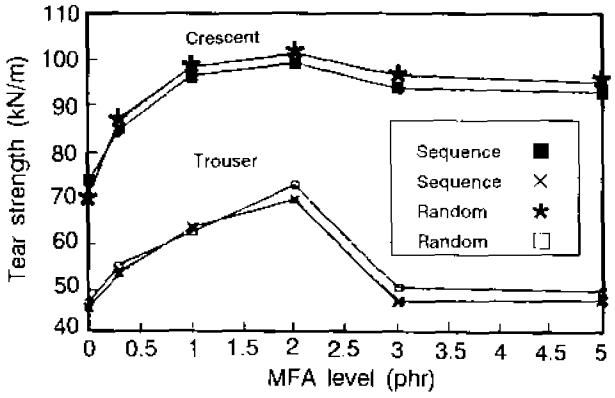


Figure 3. Tear strength versus MFA level for random and sequence mixing for NR/CB N330 mixes.

show optimum values at the level of 2 phr of MFA for all three different double strain amplitudes (DSA's) as shown in Figure 5.

Most of the mechanical properties change with increasing MFA level and this can be explained qualitatively by changes at the rubber-MFA-carbon black interfaces, as shown in Figure 6. For the control compound (0 phr MFA) there is 100% of rubber-carbon black interface due to the absence of MFA. As the MFA level increases from 0 to 2 phr, there will be a progressive decrease of rubber-carbon black interfacial area and an increase in carbon black-MFA and MFA-rubber interface. However, from carbon black dispersion test results [1], the addition of MFA from 0 to 2 phr also improves carbon black dispersion, which

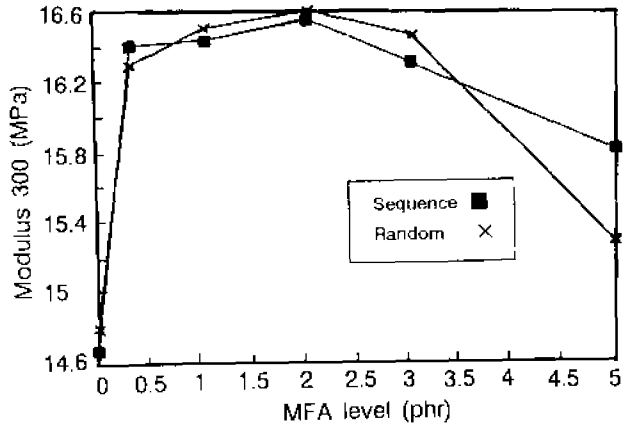
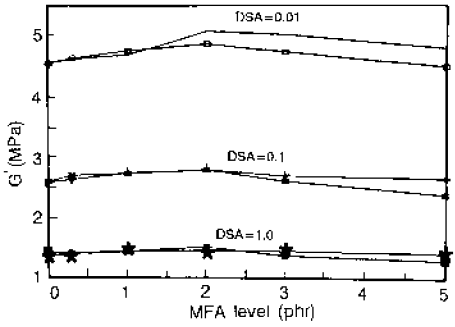


Figure 4. Modulus 300 versus MFA level for random and sequence mixing for NR/CB N330 mixes.



– Sequence + Sequence, ★ Sequence, ⋯ Random, × Random, ■ Random

Figure 5. In-phase shear modulus versus MFA level for random and sequence mixing for NR/CB N330 mixes

contributes to enhanced mechanical properties. At 2 phr of MFA, the carbon black surface completely covered by a monolayer of MFA [1,2] and this is the critical level where most of the optimum mechanical properties occur. At this stage, there is no rubber-carbon black interface or MFA-MFA layer present. As the MFA level is increased above 2 phr, there will be an increasing degree of MFA-MFA interface and this phenomenon is responsible for the reduction of the mechanical properties. Figure 7 shows the proposed mechanism of MFA

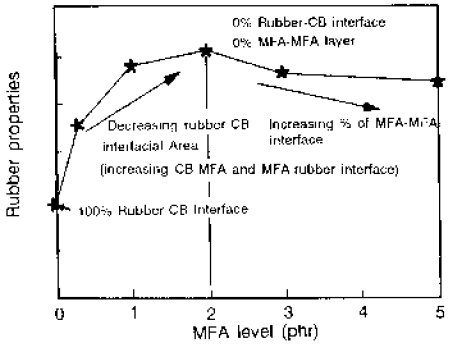
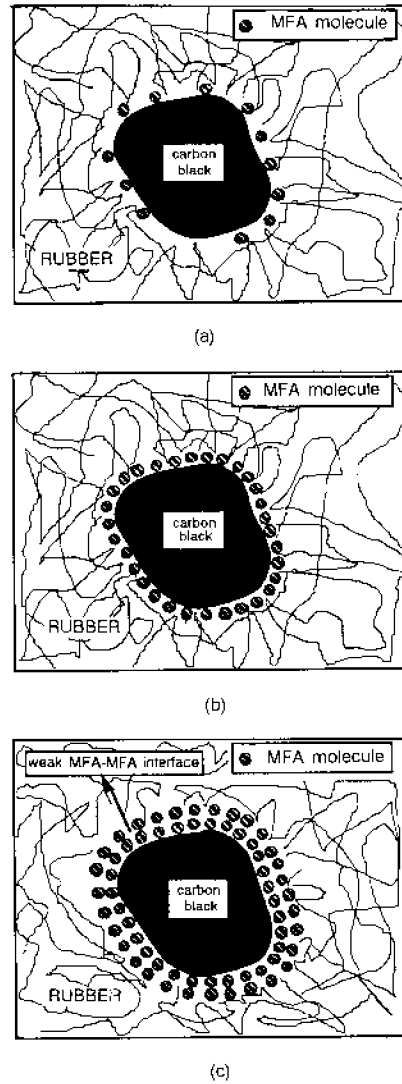


Figure 6. A qualitative interpretation at the rubber-carbon black interface with the presence of MFA to explain the changing in rubber properties.



(a) At less than a monolayer coverage: partial coverage of carbon black surfaces by MFA molecules, (b) At monolayer coverage: complete coverage of carbon black surfaces by MFA molecules, (c) At more than a monolayer coverage: formation of second MFA layer. Poor MFA-MFA interaction results in deterioration properties.

Figure 7. Mechanism of MFA adsorption at the CB-rubber interface [4].

adsorption at the carbon black-rubber interface [4].

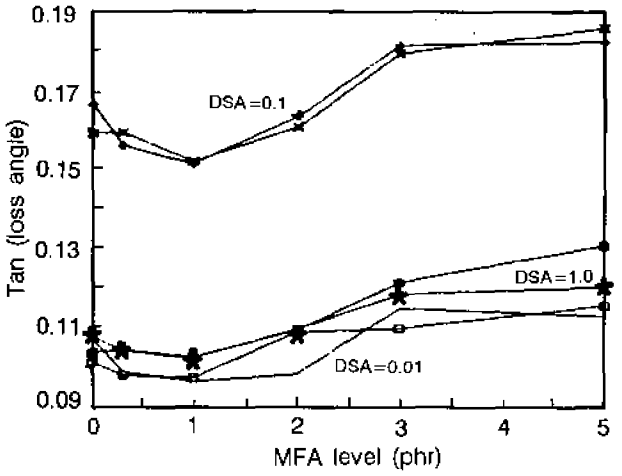
In Figure 8 both random and sequence mixing show that although the optimum properties (vulcanizate and dynamic) are at the level of 2 phr of MFA, the lowest tangent of loss angle (tan δ) is obtained for the mixture with 1 phr of MFA. It is proposed that from 0 to 1 phr of MFA reduction of tan δ is due to improvement in carbon black dispersion which is the dominant mechanism. At MFA levels greater than 1 phr, the further improvement of dispersion is relatively small and the increase in energy dissipation due to the increase MFA-rubber interlayer becomes the dominant mechanism. As the coverage of the carbon black surface by the MFA increases, the energy of interaction between the rubber and the carbon black decreases. Calculation [5] has shown that the presence of the MFA at the interface weakens the interfacial interaction by approximately 30%. Hence, it is proposed that MFA results in a new energy dissipation mechanism. The detachment of rubber molecules from MFA layer and re-attachment or slippage of rubber molecules from MFA layer is easier than with a simple NR-carbon black interface. This energy dissipation process is responsible for the increase in tan δ after 1 phr of MFA.

SEM Micrographs

The SEM micrographs at magnification $\times 300$ showed similar results as for the sequence mixing (Figure 9). The control compound surface shows a large number of undispersed carbon black aggregates. The surface for the mix containing 0.3 phr of MFA displays a few and smaller undispersed carbon black aggregate. However an improvement in carbon black dispersion can be seen for mixtures containing MFA from 1.0 to 5 phr, as the surfaces display an increasingly homogeneous microdispersion of carbon black aggregates.

CONCLUSION

The results obtained from random mixing have shown that the addition of MFA in carbon black filled NR compounds improves mechanical properties up to a critical level (2 phr). The formation of a second MFA layer at the rubber-carbon black interface is responsible for the reduction of mechanical properties beyond the critical level and at the same time, increases the hysteresis (tan δ).



– Sequence, + Sequence, * Sequence, □ Random, × Random, ■ Random.

Figure 8. The tan δ versus MFA level for random and sequence mixing.

Because the order of mixing has been randomized and the relationship between MFA concentration and mechanical properties (i.e. tensile strength, tensile modulus, tear strength and dynamic in-phase shear modulus) shows the similar trend as in sequence mixing, it clearly shows that these results confirm the previous works using the sequence mixing.

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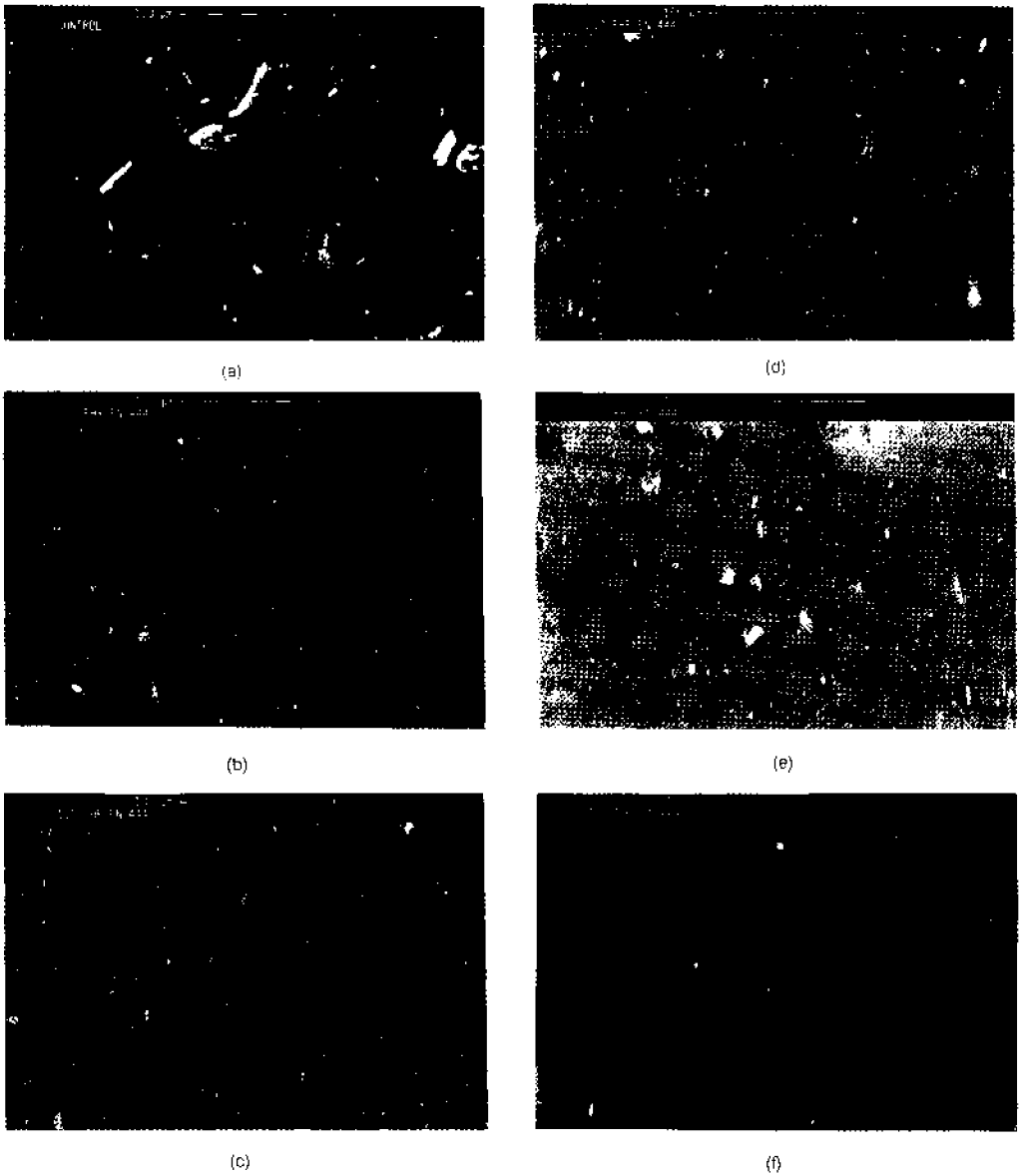

(a) (d)

(b) (e)

(c) (f)

(a) Rough surface with a large amount of undispersed carbon black, (b) Rough surface with smaller undispersed aggregates, (c) and (d) Very few and smaller undispersed aggregates. (e) and (f) Smooth surface with carbon black dispersion at the primary aggregates.

Figure 9. SEM micrographs of six NR/CB N330 mixes filled with different levels of MFA at magnification (×300): (a) 0.0 phr (control), (b) 0.3 phr, (c) 1.0 phr, (d) 2.0 phr, (e) 3.0 phr (f) 5.0 phr.

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