

The Effect of a Cationic Surfactant on the Processing and Mechanical Properties of Styrene Butadiene Rubber

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ABSTRACT

The effect of a multi-functional additive (MFA), such as N-tallow-1,3-diamine salt of a carboxylic acid on the mechanical properties of styrene butadiene rubber (SBR) peroxide system is studied. The addition of the MFA is found to improve the mechanical properties of SBR/peroxide system. Carbon black dispersion measurement using scanning electron microscopy and internal mixer power trace show that the MFA improves carbon black dispersion by acceleration of the incorporation of mixing. The MFA is also found confer higher crosslink density.

Key Words: cationic surfactant, mechanical properties, styrene butadiene rubber, dispersion, peroxide cross linking system

INTRODUCTION

It has been found that N-tallow propane-1,3-diamine salt of a carboxylic acid having the general formula $[\text{RNH}_2^+(\text{CH}_2)_3\text{NH}_3^+][\text{R}'\text{COO}^-]_2$ enhances the mechanical properties of carbon black filled natural and synthetic rubbers [1]. This surfactant has been called a multi-functional additive (MFA) since it is observed that it can function as a processing aid, a filler dispersant, a cure accelerator and a mould-release agent.

In previous works [2,3] the addition of a MFA (Akzo EN 444) to natural rubber (NR) (SMR 20) compound with 50 phr of N330 carbon black was shown to increase mechanical properties and in-phase dynamic shear modulus (G') up to a

level of 2 phr, after which there is a gradual deterioration of these properties. The reduction of properties after 2 phr is attributed to the formation of weak MFA-MFA interface which reduces the carbon black-rubber interaction. Calculation shows that 2 phr of MFA corresponds approximately to the amount needed for monolayer surface coverage of 50 phr carbon black (CB) with a specific surface area of $78\text{m}^2/\text{g}$ as measured by nitrogen adsorption [3].

It was considered that the non-rubber constituents of natural rubber could react with MFA to produce the observed effects on properties. Therefore, it was decided to devise an experiment in which a pure elastomer was used to determine if impurities in the rubber or the

components of the conventional sulphur vulcanization system show a significant effect. In this work a solution SBR (i.e., styrene butadiene rubber produced by solution polymerization) with a peroxide crosslinking agent system has been selected. This polymer is deemed to be a reasonably clean conventional system, i. e., with only a small amount of polymerization detritus left in the finished polymer and the cure system is very simple without the presence of complex organic chemicals. Two mixes, one control compound (0 phr MFA) and the other with 2 phr of MFA were prepared and their mechanical properties were compared. Two phr of MFA are taken because results from previous work [2,3] on NR compound with 50 phr of carbon black showed that optimum mechanical properties were obtained at this level.

EXPERIMENTAL

The formulation used in this work is shown in Table 1. All the rubber mixes were prepared in Francis Shaw K1 Intermix. The mixing cycle and mixing conditions used are shown in Table 2.

The test procedures used conformed to BS 1674 and BS 903 series for specimen preparation and physical properties measurement. For dynamic

Table 1. Basic formulation and properties for solution of styrene butadiene rubber cured with dicumyl peroxide.

	Control mix	MFA mix
SBR Solution (Europrene 1205)	100	100
Carbon black (N330)	50	50
Dicumyl peroxide (Di-Cup R)	1.8	1.8
MFA (EN 444)	—	2.0
Max.torque (NM) [Ⓢ]	2.63	2.55
Min.torque (NM)	0.33	0.12
Scorch time, t_5 (sec)	44	32
95% Cure, t_{95} (sec)	584	374
Tensile strength (MPa)	12.0	15.1
100% Modulus (MPa)	6.3	7.4
Elongation at break (%)	174	184

properties, a Dartec Servo Hydraulic Testing Machine was used with double strain amplitudes (DSA's) from 0.001 to 1 and a constant frequency of 1 Hz. The test used was of circular cross section. Transfer moulding was used to produce the double shear test pieces, with rubber disc dimensions of 32mm diameter and 8mm thickness.

All test samples were cured to the 95% level, as determined by a Wallace Precision Cure Analyzer.

For the carbon dispersion measurement with scanning electron microscopy (SEM), samples were cut using a new degreased razor blade on the end of a vertical sliding post. After being sputter coated with gold to avoid electrostatic charging and poor image resolution, the cut surfaces were examined by scanning electron micrograph (SEM) at a low magnification (x900) and a high magnification (x10K)

RESULTS AND DISCUSSION

Crosslinking Characteristics

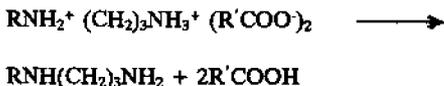
Table 1 shows that the inclusion of the MFA enhances the rate and state of cure as the mix with 2 phr of MFA has shorter t_5 and t_{95} compared to control. The reduction of the scorch and cure time in MFA compound was attributed to the production of a diamine, resulting from the decomposition of MFA molecules at the cure temperature (160°C), which is higher than the MFA decomposition temperature [4]. The

Table 2. K1 mixing cycle used for solution of styrene butadiene rubber cured with dicumyl peroxide[Ⓢ].

Time (sec)	Actions
0	Elastomer
120	All carbon black + MFA
240	Dicumyl peroxide
320	Dump

[Ⓢ]Mixing condition: rotor speed=36 rpm, fill factor=0.6, water temperature=350 °C, and dump temperatures: control=146 °C, MFA mix (2phr)=135 °C., SBR solution: Europrene 1205, Dicumyl peroxide: DI-CUP R

decomposition of the MFA proceeds as follows:



It has been demonstrated that the diamine can act as a vulcanization activator or accelerator, while the carboxylic acid can act as an internal flow additive and a mould release agent in sulphur cure system [1]. The mix with 2 phr of MFA also has higher crosslink density (maximum torque - minimum torque) than with the control compound. A further indication that inclusion of MFA has resulted in better crosslink density is shown in the plot of in-phase shear modulus, G' versus MFA level for NR gum compounds in Figure 1 [5]. It can be seen that as MFA level increases from 0.3 to 2 phr, G' increases up to maxima and starts to decrease as the level of MFA is increased further. The increase up to 2 phr is attributed to higher crosslink density caused by the presence of MFA. Grishin *et al.* [6] found that the adsorption of surfactants (poly (ethylene glycol) ethers) of n-alcohols [C_nE_m , $n = 9-18$, $m = 5-40$] on the carbon and the accelerated formation of the polysulphide fragment of accelerator, the crosslinking precursor, increases the crosslinking degree in the interface and the intensity of interfacial interaction in filled rubber. It is expected that the MFA would act in a similar way

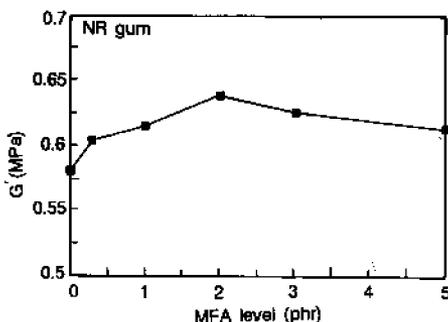


Figure 1. In-phase shear modulus versus MFA level for NR gum at DSA 0.1.

to the above surfactant, to produce the observed increase in crosslink density. From Table 1 it can be seen that peroxide cure is accelerated by MFA but, at the moment, we do not know the actual mechanism. As in CB compounds [3], when excessive MFA is used ($>2\text{phr}$), the G' starts to decrease. Excessive MFA may produce a weak boundary layer at the interface between the rubber and the carbon black coated with a monolayer of MFA, thus reducing the mechanical properties.

Mechanical Properties

Table 1 shows that the mix with 2 phr of MFA has a higher tensile strength and stress at 100% strain (M100) compared to the control. As for M100, the mix with 2 phr of MFA also has higher, in-phase shear modulus, G' (Figure 2). However, in terms of hysteresis ($\tan \delta$), the control mix has a lower value compound with MFA (Figure 3).

Calculation [3] shows that the presence of MFA at the interface weakens the interfacial interactions between the carbon black and rubber by approximately 30%. Hence, it is proposed that MFA results in a new energy dissipation mechanism. The greater frequency of detachment of the rubber molecules from the MFA layer re-attachment or slippage of rubber molecules is easier than with a simple SBR-CB interface. This energy dissipation process results in a higher $\tan \delta$ for the compound with MFA compared to control

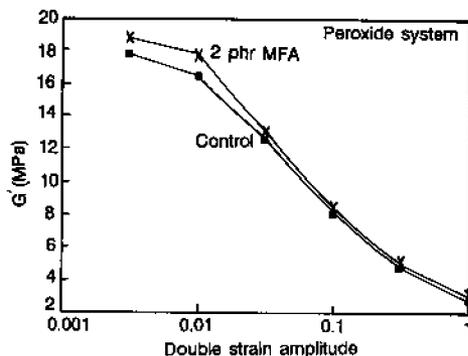


Figure 2. Relationship between G' and DSA for SBR/CB N330 mixes with and without MFA.

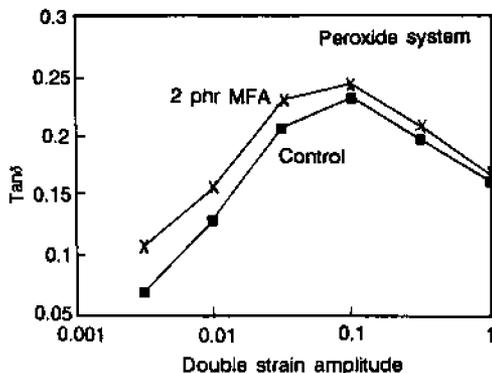


Figure 3. Tan δ (loss angle) versus DSA for SBR/CB N330 mixes with and without MFA.

compound.

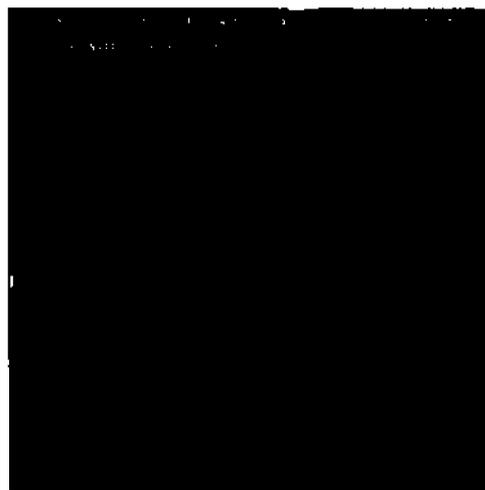
Dispersion Test

The surface of the control compound shows carbon black agglomerates and vacuole formation resulting from dewetting of carbon black agglomerates and these phenomena contribute to the lower vulcanizate properties for the control mix. The mix with 2 phr of MFA displays a smooth surface with homogeneous microdispersion of carbon black aggregates (Figures 4 and 5 of SEM pictures).

Results from carbon black dispersion test above have shown that one of the main MFA actions in carbon black filled rubber compound is the improvement of filler dispersion at constant mixing time. This is achieved by acceleration of the incorporation stage of mixing. Evidence for the acceleration of incorporation is provided by the internal mixer power trace in Figure 6. This figure shows a much more rapid rise of power following the filler addition when the MFA is used. Thus, when MFA is present, the number of rotor revolutions available for disagglomeration is increased compared to the control compound. The dump power for the compound containing 2 phr of MFA is lower than the control compound which shows that better state of cure is achieved when MFA is present. This again proves that the better dispersion is obtained when MFA is used.



Control

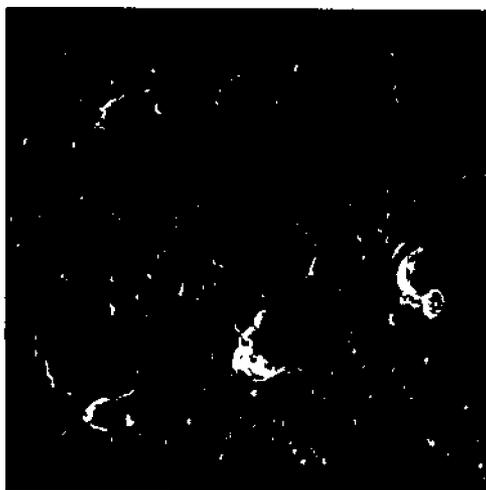


2 phr MFA

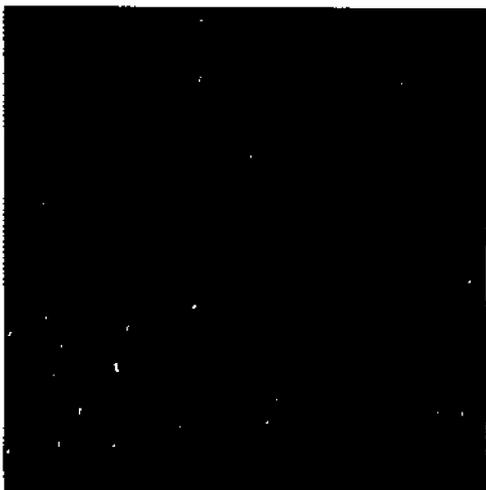
Figure 4. SEM micrographs of sol.SBR (Europrene 1205) /peroxide system for control and 2 phr of MFA mixes at low magnification (x900).

Control: Surface displays a large number of vacuole formation with relatively a larger size of carbon aggregates.

2 phr MFA: Carbon black dispersion at primary aggregates



Control



2 phr MFA

Figure 5. SEM micrographs of sol.SBR (Europrene 1205) /peroxide system for control and 2 phr of MFA mixes at high magnification (x10K).

Control: Many lumps of carbon black aggregates and vacuole formation resulting from dewetted of carbon black aggregates.

2 phr MFA: Homogeneous microdispersion of carbon black aggregates.

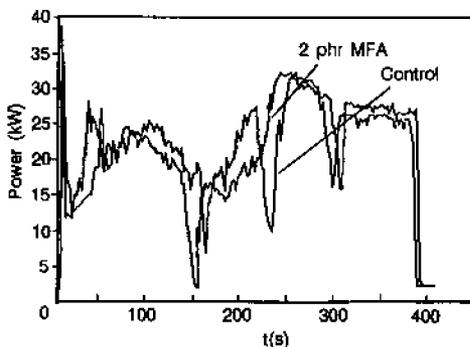


Figure 6. Power versus mixing time for SBR/CB N330 mixes with and without MFA.

CONCLUSION

The results from above confirm the previous work [2,3] that multi-functional additive (MFA) has the ability to increase mechanical properties (e.g., tensile strength, tensile modulus and in-phase shear modulus, G') compared to control. The enhancement of these properties is attributed solely to the inclusion of MFA because the work is carried out based on a "clean" system. The addition of MFA results in better carbon black dispersion and higher crosslink density.

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