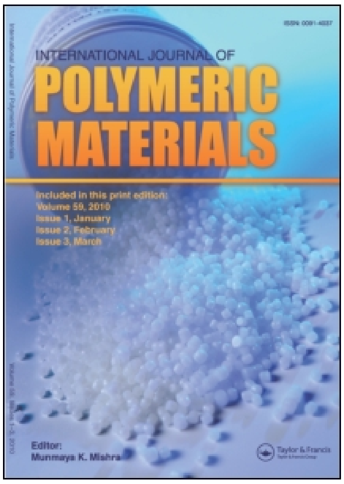

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The Effect of Multifunctional Additive on Dynamic and Physical Properties of Natural Rubber Gum Compounds

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The paper reports the effect of multifunctional additive (MFA) on dynamic and physical properties of natural rubber gum compounds. As the MFA level increased, the maximum elastic torque (S′@MH) increased whereas the minimum elastic torque (S′@ML) decreased. Compared to the control compound (without MFA), the incorporation of MFA significantly reduced the viscous torque (S″@MH) and tan δ @MH especially below level of 2 phr. It was also found that to obtain better physical properties *viz.* tensile strength, tensile modulus and tear strength, the use of MFA at 2 phr is recommended.

Keywords: Multifunctional additive; dynamic properties; physical properties; natural rubber; curing characteristics

1. INTRODUCTION

In 1983, Hepburn and Mahdi [1] have discovered a class of surfactant plasticiser with a multipurpose action. These materials–SAPA, for convenience–function as internal processing agents during conventional rubber processing (in the 30° to 100°C range) but dissociate at the higher temperatures used for vulcanization (over 140°C) to form secondary amines with act as cure accelerators. These SAPA's were a type of cationic surfactant whose general structure is $[R'NH_2(CH_2)_3NH_3]^{2+} \cdot 2[C_{17}H_{33}COO]^-$. Since their initial discovery the term Multi Functional Additive (MFA) has replaced the original name to better describe the wider properties these materials were found to possess as rubber compounding ingredients [2].

In our previous works [3 – 6], we reported the use of MFA in carbon black and silica filled natural rubber compounds. The addition of MFA to a natural rubber compound with 50 phr of N330 carbon black was shown to increase physical properties up to a level of 2 phr, after which there was a gradual deterioration of properties. For silica filled natural rubber compounds, the optimum level of MFA to obtain maximum mechanical properties were in the range of 5 – 7 phr, approximately two times higher then those which would be needed for monolayer coverage of carbon black with similar total surface area. In this study, the effect of similar commercial MFA (EN 444) on dynamic and physical properties of natural rubber gum compounds will be reported.

2. EXPERIMENTAL

2.1. Compounding Ingredients, Formulations and Mixing Procedure

Table I shows the raw materials and formulation used in this study together with the suppliers. Mixing was carried out on a laboratory size (160 × 320 mm) two roll mixing mill (Model XK-160) in accordance to the method described by ASTM D 3184.

TABLE I Natural rubber gum compounds with different levels of MFA

Ingredients	*Supplier*	*Formulation (phr)*
Natural rubber (SMR L)	RRIM[a]	100.0
Stearic acid	Bayer (M) Ltd	3.0
Flectol H[b]	Monsanto (M) Ltd	1.0
CBS[c]	Bayer (M) Ltd	0.5
Sulphur	Bayer (M) Ltd	2.5
Zinc oxide	Bayer (M) Ltd	5.0
MFA (EN 444)[d]	Akzo Chemical (U.K)	0.0, 0.3, 1.0, 2.0, 3.0, 5.0

[a] Rubber Research Institute of Malaysia.

[b] Poly-1,2-dihydro-2,2,4-trimethylquinoline.

[c] *n*-cyclohexylbenthiazyl sulphenamide.

[d] *n*-tallow-1,3-propanediamine distearate.

2.2. Measurement of Curing Characteristics and Dynamic Properties

The MDR 2000 moving die rheometer (MDR), a rotorless curemeter, has gained much acceptance by the rubber industry since its introduction in 1988. In many cases, this instrument is replacing the oscillating disk rheometer (ODR) as described in ASTM standard Test Method D2084. The dynamic properties before, during and after cure were studied at 140°C. A unique signal processing system and Fourier transform software separates the complex torque into elastic torque (S') and viscous torque (S''). The tan delta is derived by diving S'' by S'. In addition to the dynamic properties, the MDR gives digital outputs of curing characteristics such as scorch times, cure times, cure rates and torque values.

2.3. Physical Properties

The vulcanizates were tested for different physical properties according to respective ASTM standards. Tensile and tear properties were studied using an Instron Universal Testing Machine, model 1114 at a crosshead speed of 50 cm/min. For tensile properties, samples were punched out using die E from moulded sheets and were tested according to ASTM D 412 method A. For tear strength measurements, standard test pieces (ASTM D 624–Type C) were used.

2.4. Determination of Crosslink Density

Cure test pieces of dimension 30 mm × 5 mm × 2 mm were weighted using an electrical balance and each test piece was immersed in a glass vessel containing toluene (30 cc) at 25°C. The vessels were kept in the dark to prevent oxidation. The samples were then removed from glass vessels and excess toluene removed by lens blotting paper. The samples were then placed in a closed vessel, to prevent toluene evaporation and the weight of the swollen samples were determined. The sample was then reimmersed in the toluene and the process was repeated until a constant swollen weight could be obtained. The sample was de-swollen in a vacuum at room temperature to a constant weight in order to find the volume fraction of toluene adsorbed in the rubber. Crosslink density of samples was determined by using Flory–Rehner equation

[7] (Eq. (1)). Physical crosslink density $(2M_c)^{-1}$ was related to volume fraction of rubber in swollen gel by solvent by equilibrium (V_r).

$$-\ln(1-V_r)-V_r-XV_r^2=2P_{\mathrm{RN}}V_o(2M_c)^{-1}V_r^{1/3} \tag{1}$$

where V_r = volume fraction of swollen rubber at equilibrium
X = interaction constant characteristic between rubber sample and toluene (0.39)
P_{RN} = rubber network density
= 0.932 at 35°C
V_o = molar volume of the toluene
= 108.05 at 35°C

By using Flory–Rehner equation, $(2M_c)^{-1}$ value obtained.

3. RESULTS AND DISCUSSION

The effects of MFA level on the maximum elastic torque (S′@MH) and minimum elastic torque (S′@ML) are shown in Figures 1 and 2. It can be seen in Figure 1 that the S′@MH increased with increasing MFA level. According to Lee [8] and Dick [9], S′@MH generally correlates with durometer hardness or cure modulus. From Figure 1, it is clear that the incorporation of MFA improved the modulus of the rubber vulcanizates. Results from tensile modulus *i.e.*, modulus at 100% elongation (M100) and modulus at 300% elongation in Figure 3 support this observation.

Figure 2 shows that the S′@ML decreased with increasing MFA level. It is well accepted that S′@ML is a measure of compound viscosity [8] and also provide valuable information about compound processability [9]. This indicates that the compound viscosity and processability were improved with the addition of MFA.

According to Abidin *et al.* [10], the use of MFA reduced the viscosity of the rubber compounds, improved extrusion by increasing the shear rate prior to the onset of melt fracture and can also gave improvements in mould release.

Figure 4 shows the torque difference, S′@MH-S′@ML (max. elastic torque – min. elastic torque) of the compounds increased with increasing MFA level. The increment in the torque difference values indicates that MFA has an activating effect to cause more efficient use of sulphur

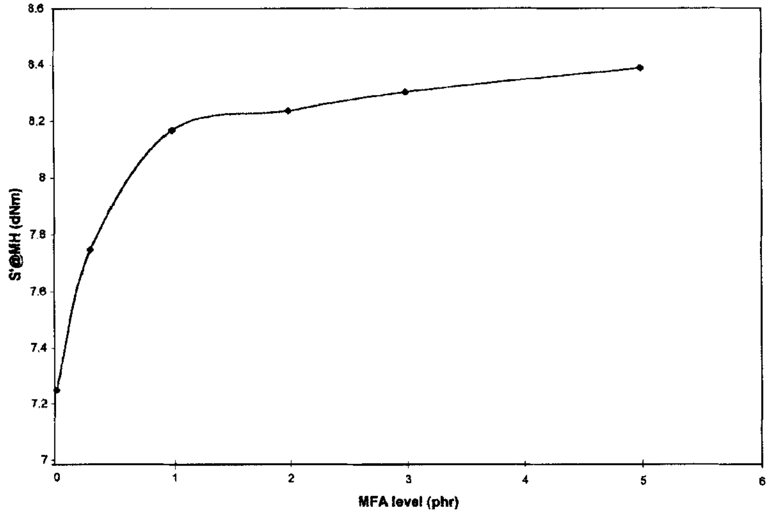

FIGURE 1 The effect of MFA level on the S′@MH of natural rubber gum compounds.

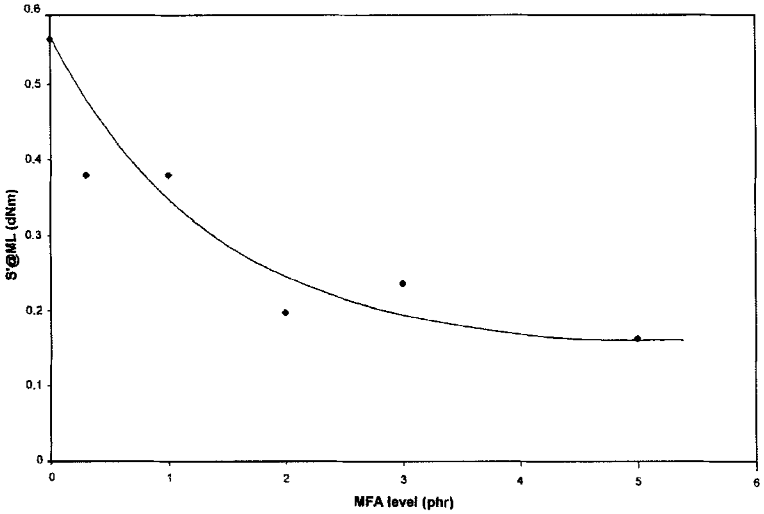

FIGURE 2 The effect of MFA level on the S′@ML of natural rubber gum compounds.

for higher degree of crosslinking. Results from swelling measurement in Figure 5 support this observation.

Figures 6 and 7 show the effect of MFA level on the viscous torque (S″@MH) and tan δ @MH. Viscous torque relates to the damping

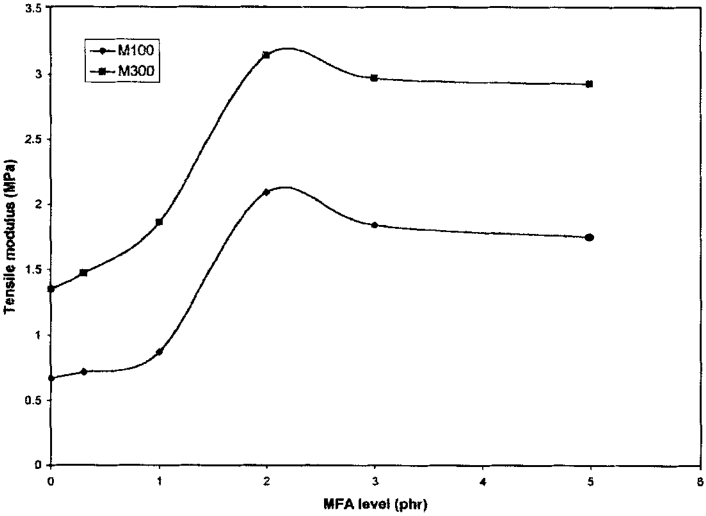

FIGURE 3 The effect of MFA level on the tensile modulus of natural rubber gum compounds.

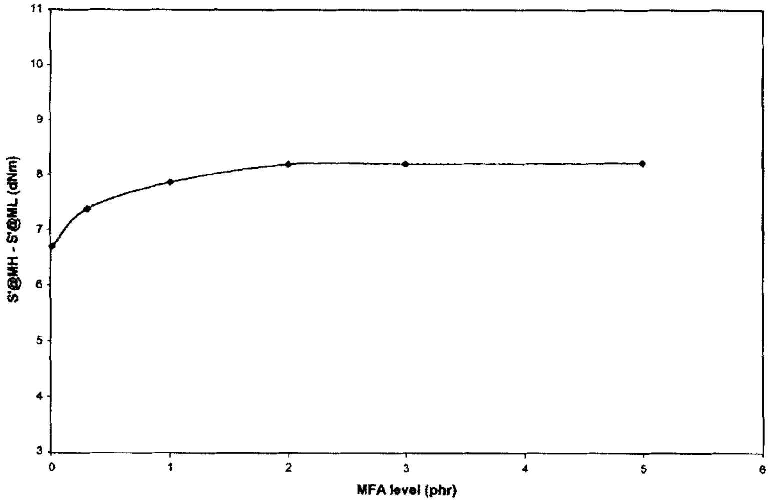

FIGURE 4 Relationship between S′@MH-S′@ML and MFA level of natural rubber gum compounds.

characteristics of a rubber compound whereas the lower tan δ for a cured compound, the greater its resiliency [9]. From Figures 6 and 7, compared to control compound (0 MFA), the decrease in S′@MH and tan δ @MH is quite significant especially below 2 phr of MFA. More

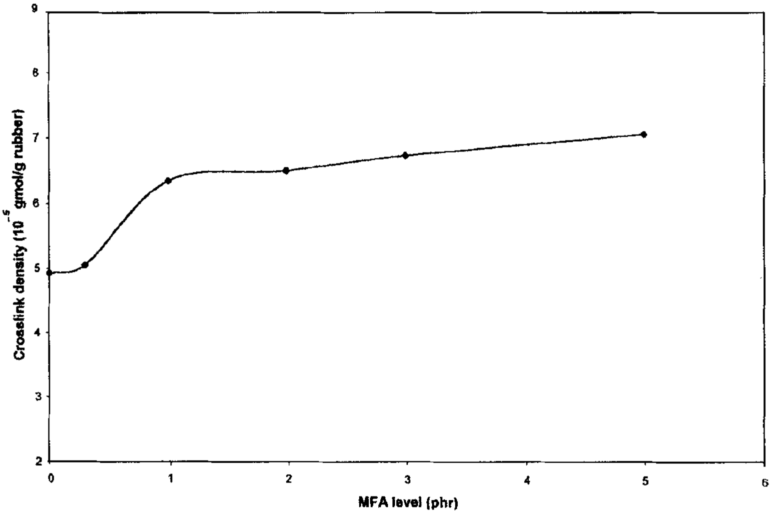

FIGURE 5 Variation of crosslink density with MFA level of natural rubber gum compounds.

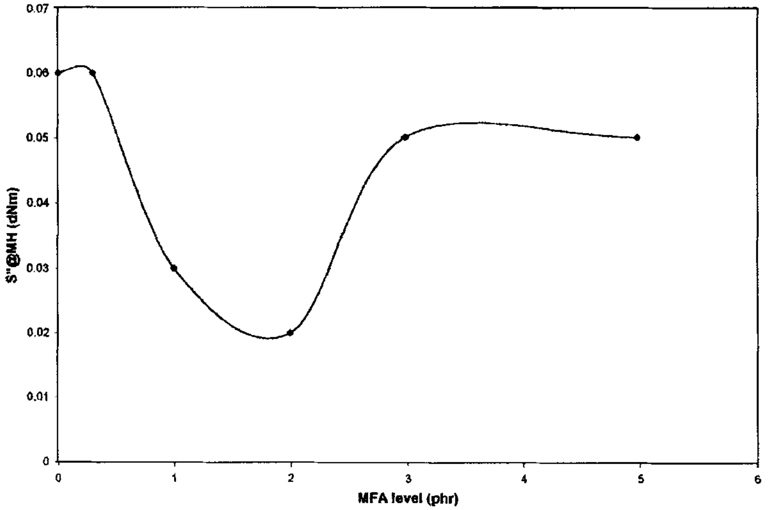

FIGURE 6 The effect of MFA level on the S"@MH of natural rubber gum compounds.

than 2 phr *i.e.*, at 3 and 5 phr of MFA the decrease in both properties is small.

The effect of MFA level on scorch time, t_2 and cure time, t_{90} is shown in Figure 8. It can be seen that the incorporation of MFA en-

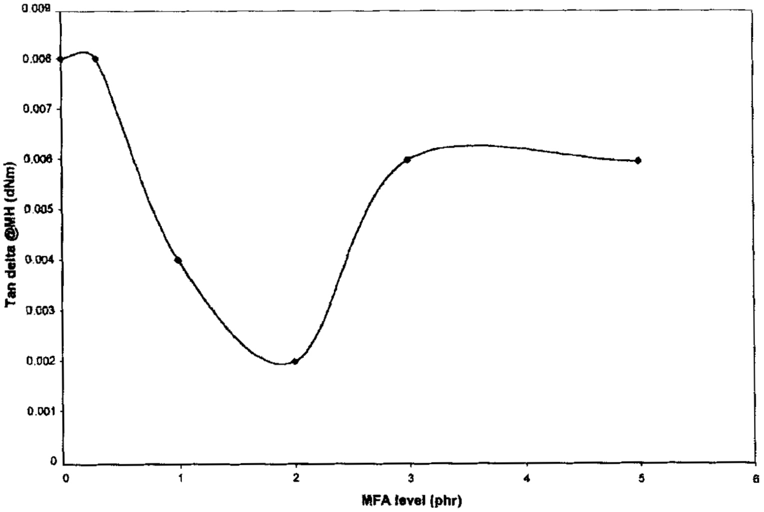

FIGURE 7 The effect of MFA level on the tan delta @MH of natural rubber gum compounds.

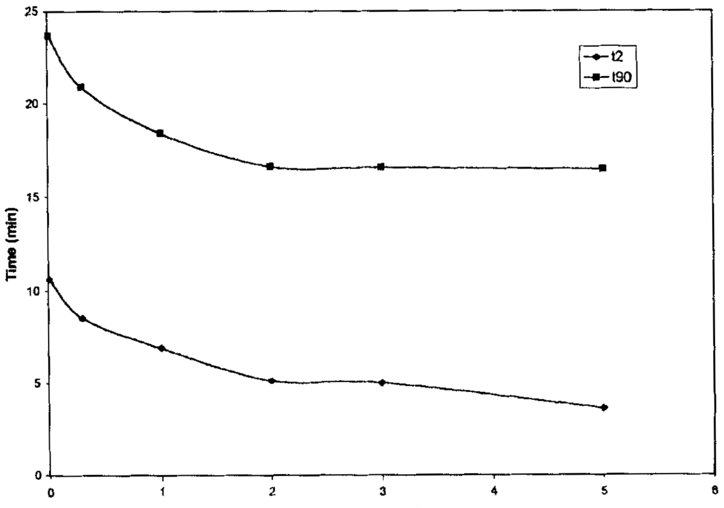

FIGURE 8 The effect of MFA level on the t_2 and t_{90} of natural rubber gum compounds.

hances the rate and state of cure of the rubber compounds. The reduction of the t_2 and t_{90} with the incorporation of MFA was attributed to the production of diamine, resulting from the decomposition of MFA molecules at the cure temperature (140°C) which is higher than the MFA decomposition temperature [11]. 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 [12]. It is well established [13–15] that certain organic substances containing nitrogen atoms promote the vulcanization of olefinic rubber comprising sulphur and primary accelerators through the formation of complexes which are responsible for the fission of sulphur molecules to form crosslinks between the linear rubber chains.

Figure 9 shows the relationship between tensile and tear strengths with MFA level. It can be seen that both properties increased up to MFA level of 2.0 phr after which the properties start to decrease. Results for tensile modulus in Figure 3 also exhibit similar trend. However compared to control compound, compounds with 3 and 5 phr of MFA still have higher tensile strength, tensile modulus and tear strength. The deterioration of these properties after 2 phr of MFA was

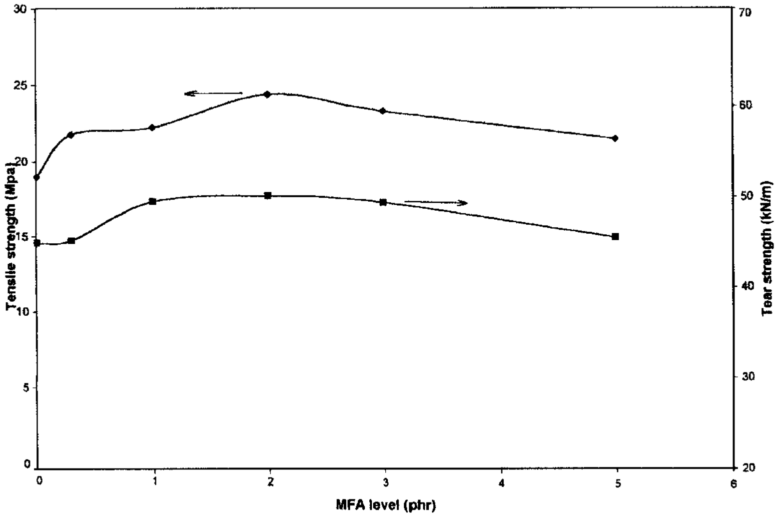

FIGURE 9 The effect of MFA level on the tensile and tear strengths of natural rubber gum compounds.

due to the weak boundary layer at the rubber MFA interphase as a result of the plasticizing effect *i.e.*, internal slippery of excessive MFA molecules [6]. To achieve the best physical properties, MFA should be used at the level of 2 phr.

4. CONCLUSIONS

The incorporation of MFA into the natural rubber gum compounds improved the processability and reduced the viscosity of the rubber compounds. The scorch and cure times were reduced with increasing level of MFA. The incorporation of MFA up to 2 phr was found to increase the physical properties of the natural rubber gum compounds.

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