

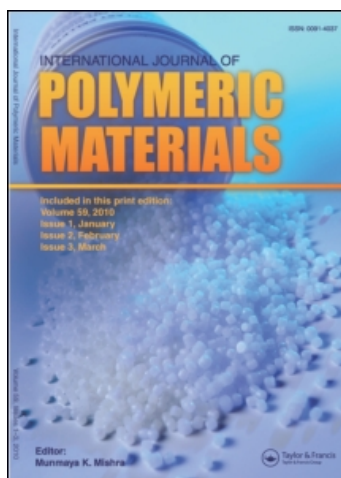
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Palm Oil Fatty Acid as an Activator in Carbon Black Filled Natural Rubber Compounds: Effect of Epoxidation

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The effect of palm oil fatty acid on curing behaviour and mechanical properties of epoxidized natural rubber (ENR 25 and ENR 50) and one grade of unmodified natural rubber (SMR L) was investigated in the concentration range of 0 to 7.0 phr. Results indicate that scorch and cure times increase with palm oil fatty acid concentration for all the rubbers investigated. At a similar palm oil fatty acid concentration, ENR 50 showed shortest scorch and cure times followed by ENR 25 and SMR L. Tensile modulus and hardness of all rubbers also increase with increasing acid concentration. At a similar acid concentration, ENR 50 showed the highest tensile modulus and hardness followed by ENR 25 and SMR L. However, the tensile and tear strengths pass through a maximum with increasing acid concentration but at a similar acid concentration, SMR L showed the highest tensile and tear strengths compared to ENR 25 and ENR 50.

Keywords: Palm oil fatty acid; curing behaviour; mechanical properties; carbon black; epoxidized natural rubber

1. INTRODUCTION

Epoxidized natural rubber (ENR) is a rubber having properties resembling those of synthetic rubbers rather than natural rubber [1–2]. The presence of the oxirane groups make it possible to perform various types of crosslinking reactions in addition to normal sulphur vulcanization through the double bond [3–4]. Increasing epoxidation

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increased the glass transition temperature, which resulted in decreased resilience (more damping), reduced air permeability, higher hysteresis, and better wet fraction. Some of these properties have even been proclaimed to be superior to those of some popular synthetic rubbers. For example the resistance to air permeability of ENR 50 has been claimed to be comparable to butyl rubber and medium acrylonitrile-content, NBR [5–6].

In our previous works [7–8], the concentration effect of palm oil fatty acid on curing characteristics and mechanical properties of natural rubber gum compounds and calcium carbonate filled natural rubber compounds were reported. In this study, the same palm oil fatty acid and 50 phr of carbon black (N 330) in SMR L, ENR 25, and ENR 50 having 0, 25 and 50 mol% of epoxidation were examined. The effects of palm oil fatty acid concentration in these three natural rubber compounds with different degree of epoxidation will be reported.

2. EXPERIMENTAL

2.1. Materials and Formulations

SMR 10 grade natural rubber was obtained from Rubber Research Institute of Malaysia (RRIM) while epoxidized natural rubbers (grades ENR 25 and ENR 50) were supplied by the Kumpulan Guthrie (M) Ltd. Palm oil fatty acid, Palmac 770 was obtained from Acidchem (M) Ltd. Penang, Malaysia and its specification is shown in Table I. Other ingredients such as zinc oxide, sulphur, 2-mercapto benzothiazole (MBT) and poly-1,2-dihydro-2,2,4-trimethyl quinoline (Flectol H) were purchased from Bayer (M) Ltd. While carbon black, N330 was obtained from Malayan Carbon (M) Ltd. The full recipes used in this study are shown in Table II.

2.2. Mixing and Cure Characteristics Determination

Mixing was carried out on a laboratory size (160 mm × 320 mm) two roll mixing mill (Model XK-160) in accordance to the method described by the American Society for Testing and Materials (ASTM),

TABLE I Specification for palm oil fatty acid (PALMAC 770 – oleic acid 80% min) [9]

Titre °C	9 Max
Iodine value	94–102
Acid value	194–204
Colour lovibond	
5.25" Cell max	10 Yellow 1.5 Red
Typical chain length	% Composition
<i>Saturated</i>	
C _{10:0} (Caprylic acid)	
C _{12:0} (Lauric acid)	
C _{14:0} (Myristic acid)	6 Max
C _{16:0} (Palmitic acid)	
C _{18:0} (Stearic acid)	
<i>Unsaturated</i>	
C _{18:1} (Oleic acid)	80 Min
C _{18:2} (Linoleic acid)	14 Max

TABLE II Typical formulations

Materials	phr
Natural rubber ^a	100
Carbon black (N330)	50
Zinc oxide	5.0
Sulphur	2.5
MBT	1.2
Flectol H	1.0
Palm oil fatty acid	0.0, 1.0, 3.0, 5.0, 7.0

^a Three types of natural rubber were used viz. SMR L, ENR 25 and ENR 50.

designation D 3184–80. The respective cure times at 140°C as measured by t_{90} were then determined using a Monsanto Rheometer, model MDR 2000. The scorch times, torque, elastic modulus *etc.*, can also be determined from the rheograph.

2.3. Measurement of Tensile Properties, Tear Strength and Hardness

The various rubber compounds were compression moulded at 140°C according to their respective t_{90} , into test specimen sheets. Dumb-bell and crescent test pieces according to ISO 37 and ISO 34 respectively were then cut out. Tests were carried out by Monsanto Tensometer, T10 according to BS 903: Part A2 and BS 903: Part A3, respectively at 500 mm/min cross-head speed. The test for hardness was carried out

by using the Shore type A Durometer according to ASTM 2240. All tests were conducted at room temperature (25°C).

2.4. Swelling Measurement

Cure test pieces of dimension 30 mm × 5 mm × 2 mm were weighed 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 deswollen in a vacuum at room temperature to a constant weight. In this study, we have determined Q (the weight of toluene uptake per gram of rubber hydrocarbon), according to the expression derived by Park and Brown [10] as shown below

$$Q = \frac{\text{Swollen weight} - \text{deswollen weight}}{\text{dry weight} \times 100/\text{formula weight}}$$

3. RESULTS AND DISCUSSION

3.1. Curing Characteristics

Tables III–V summarize the values of t_{90} , scorch time and torque values for SMR L, ENR 25 and ENR 50 vulcanizates respectively. It can be seen that $M_{HR}-M_L$ (maximum torque – minimum torque) for all rubbers increased with increasing level of acids used. From theory [11], it is known that the torque difference, $M_{HR}-M_L$ shows shear dynamic modulus which indirectly related to the crosslink density of the compound. Hence, it can be concluded that the incorporation of palm oil fatty acid has contributed to better crosslinking. Figure 1 shows the effect of palm oil fatty acid concentration on the weight of toluene uptake per gram of rubber Q . It can be seen that the Q value decreased with increasing palm oil fatty acid level. This shows that

TABLE III Cure time (t_{90}), scorch time and (maximum torque–minimum torque), M_{HR} - M_L of carbon black filled SMRL vulcanizates at different palm oil fatty acid concentrations

Palm oil fatty acid concentration (phr)	0	1	3	5	7.5
t_{90} (min)	15.00	15.25	15.75	18.00	18.75
Scorch time (min)	3.63	3.75	3.80	3.88	3.98
Maximum torque–Minimum torque (dNm)	26.0	26.5	27.5	29.5	32.5

TABLE IV Cure time (t_{90}), scorch time and (maximum torque–minimum torque), M_{HR} - M_L of carbon black filled ENR 25 vulcanizates at different palm oil fatty acid concentrations

Palm oil fatty acid concentration (phr)	0	1	3	5	7.5
t_{90} (min)	13.38	13.43	14.00	16.50	16.38
Scorch time (min)	2.05	2.10	2.25	2.50	3.10
Maximum torque–Minimum torque (dNm)	47.5	52.5	54.5	57.2	57.3

TABLE V Cure time (t_{90}), scorch time and (maximum torque–minimum torque), M_{HR} - M_L of carbon black filled ENR 50 vulcanizates at different palm oil fatty acid concentrations

Palm oil fatty acid concentration (phr)	0	1	3	5	7.5
t_{90} (min)	11.25	12.25	12.55	12.75	12.85
Scorch time (min)	1.25	1.50	1.75	1.85	2.00
Maximum torque–Minimum torque (dNm)	56.0	60.0	65.0	67.0	74.0

palm oil fatty acid has some effect on crosslink density. Barton and Hart [12] and Morre and Porter [13] in their previous works on MBT accelerated system reported that there was increment in crosslink with increasing fatty acid in rubber compounds. Higher concentration of soluble zinc stearate complex in hydrocarbon caused faster desulphuration of crosslinking and most of the crosslinking formed was mono and disulphidic.

Tables III–V also show that the effect of palm oil fatty acid on enhancement in M_{HR} - M_L is highest in ENR 50 followed by ENR 25 and SMRL vulcanizates. According to Bateman [14], at lower pH (acidic), acid catalyst epoxide ring opening reaction would occurred in ENR compounds. The highest M_{HR} - M_L for ENR 50 might be due

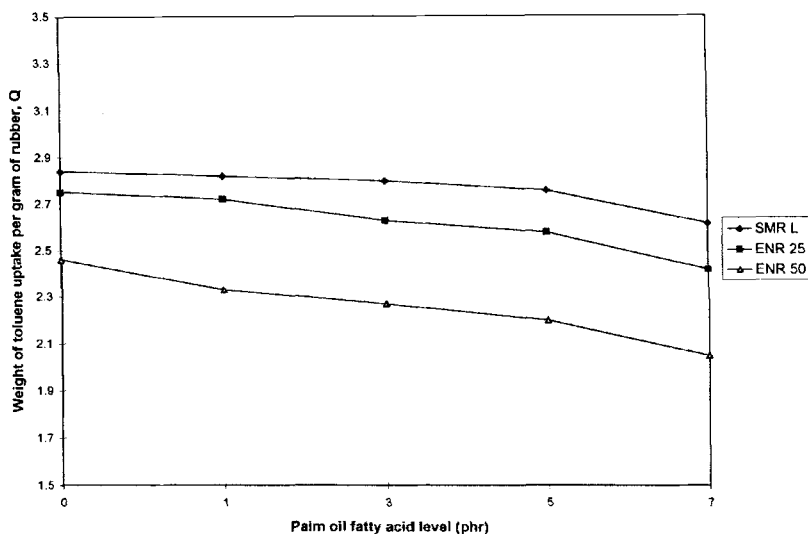


FIGURE 1 Comparison of the effect of palm oil fatty acid concentration on the weight of toluene uptake per gram of rubber in various carbon black filled natural rubber compounds.

to the acid catalyst ring-opening reactions *via* ether crosslinks during vulcanization, resulting in an increase in T_g and crosslink density [6, 15].

It can be seen from Tables III–V the t_{90} and scorch time increase with increasing acid concentration. These results show that palm oil fatty acid retards the onset of vulcanization similar to well known retarders *viz* benzoic acid [16]. Coran [17–18] found that the increased of scorch time with higher concentration of stearic acid is associated mainly with the complex formation of chelates between the zinc ion (brought into solution by stearic acid) and accelerator, intermediate reaction products or crosslink precursors.

At a similar palm oil fatty acid concentration, ENR 50 vulcanizates have the shortest scorch and cure times followed by ENR 25 and SMR L vulcanizates. This shows that the degree of epoxidation plays an important role in the curing process of the compounds. One possible explanation is that ENR contains epoxide groups that activate the adjacent double bonds, thus increasing the rate of crosslinking and subsequently, shortening the scorch time. The higher the

concentration of the epoxide group in the rubber chain, the stronger is the activation of the adjacent double bond. This is shown by the shortest scorch and cure times of ENR 50 compared to ENR 25 and SMRL compounds. Gelling and Morrison [19] found this type of additional activation when olefin and epoxide groups are in the same molecule.

3.2. Mechanical Properties

Figure 2 illustrates the modulus at 300% elongation (M300) for carbon black filled SMRL, ENR 25 and ENR 50 compounds at different palm oil fatty acid concentration. It is obvious that M300 for all rubbers increased with increasing acid concentration. Similar observation can be seen in hardness test results (see Fig. 3). According to Sloan *et al.* [20], stiffness property (modulus) and hardness are depended only on the degree of crosslink. Hardness and stiffness of rubber compounds increased with increasing the degree of crosslinking. However at a similar palm oil acid concentration, ENR 50

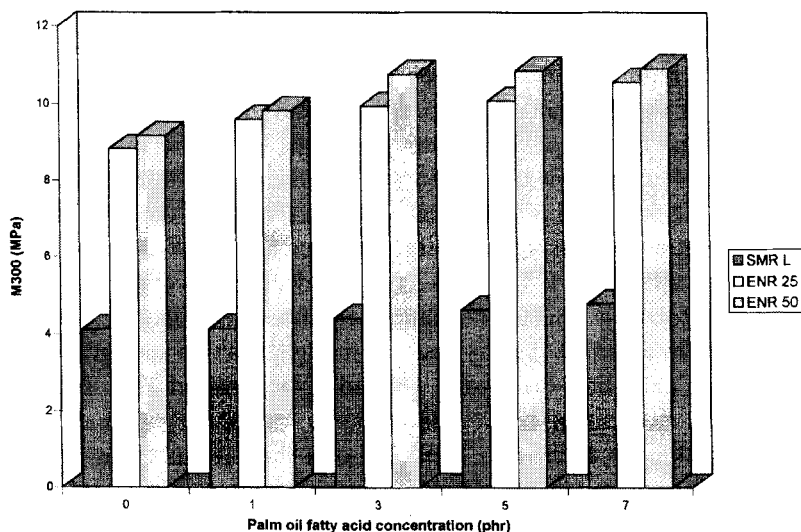


FIGURE 2 The effect of palm oil fatty acid concentration on the tensile modulus in various carbon black filled natural rubber compounds.

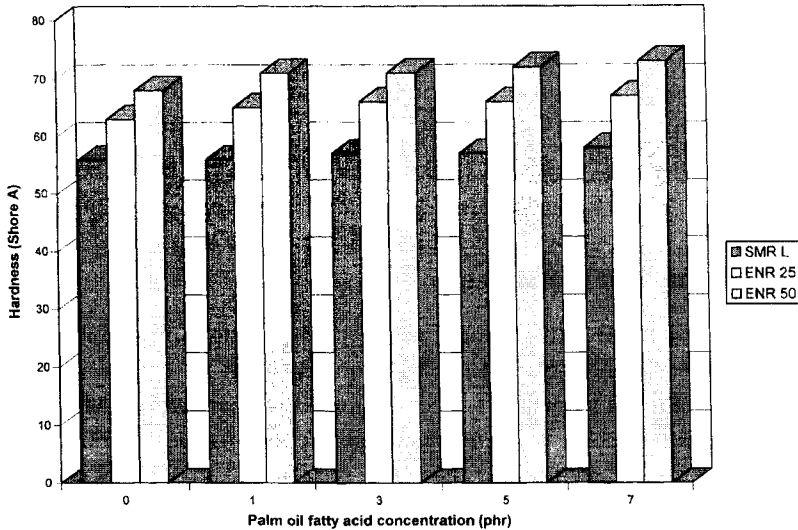


FIGURE 3 Relationship between hardness and palm oil fatty acid concentration in various carbon black filled natural rubber compounds.

compounds showed the highest hardness and modulus properties followed by ENR 25 and SMR L vulcanizates. Baker *et al.* [21–22] in their comparison of silica filled SMR L, ENR 25 and ENR 50 vulcanizates also reported the similar observation. According to them, the reaction of the sulphur acids from the oxidation of sulphides causes ring-opening of the epoxide groups and leads to ether crosslinks.

Figures 4 and 5 show that the incorporation of palm oil fatty acid to SMR L, ENR 25 and ENR 50 compounds increased the tensile and tear strengths up to maximum value and then decreased. According to Morrison and Porter [23] increment in the degree of crosslinking may be one factors contributes to enhancement in tensile strength. Actually increment in crosslink density resulted in higher tensile strength at the beginning and then decreased. Hamed [24] reported that fracture properties such as tear and tensile strengths, pass through a maximum as crosslinking is increased. Table I shows the various types of acid presence in palm oil fatty acid. After the optimum level, some of these acids would act as internal plasticiser and resulted in reduction of these properties.

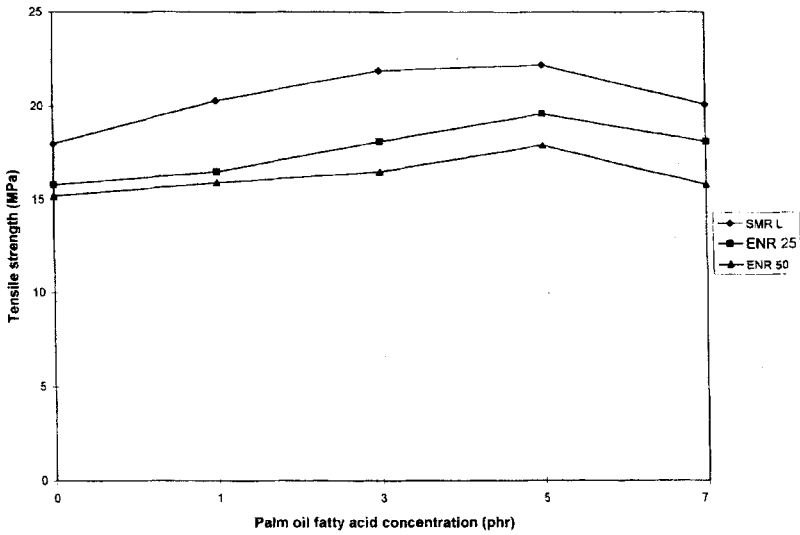


FIGURE 4 The effect of palm oil fatty acid concentration on the tensile strength in various carbon black filled natural rubber compounds.

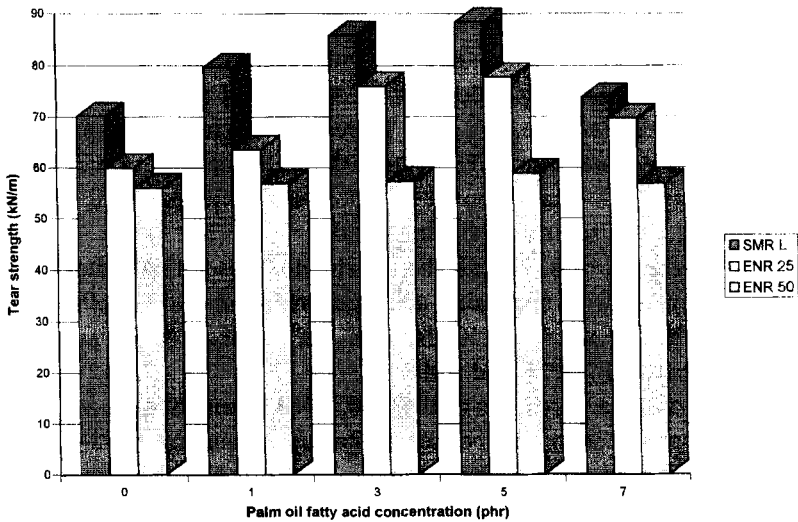


FIGURE 5 Comparison of the effect of palm oil fatty acid concentration on the tear strength in various carbon black filled natural rubber compounds.

At a similar palm oil fatty acid concentration, the tensile and tear strengths of SMRL vulcanizate is highest followed by ENR 25 and ENR 50 vulcanizates (see Figs. 4 and 5). It is well recognised that the dissipative processes which occur in rubbers are important factors in determining their strength. The strength of strain-crystallising rubbers is substantially superior to that of non or less strain crystallising materials, where the dissipative process is predominantly visco-elastic. SMRL has a stereo-regular structure and hence can undergo strain crystallisation. The epoxidation process is a stereo-specific reaction and ENR will thus retain the stereo-regular *cis* 1,4-configuration of SMRL. This mean that the ENR may also undergo strain crystallisation. However the mechanical properties of ENR 50 were significantly lower than those of NR and ENR 25. This may be due to the reduction in the degree of crystallinity as the mole % of epoxidation increased from SMRL to ENR 50.

CONCLUSIONS

1. For all the rubbers studied, scorch and cure times increase with increasing palm oil fatty acid concentration. At a fixed palm oil fatty acid concentration, ENR 50 vulcanizates show the shortest scorch and cure times followed by ENR 25 and SMRL.
2. The difference torque, $M_{HR} - M_L$ increases with increasing palm oil fatty acid concentration. This shows that the incorporation of palm oil fatty acid has contributed to better crosslinking. Results from swelling test also exhibit similar trend.
3. For all the rubbers studied, the tensile modulus (M300) and hardness increase with increasing acid concentration. At a similar acid concentration the ENR 50 exhibits the highest tensile modulus compared to ENR 25 and SMRL.
4. Tensile and tear strengths of ENR 50, ENR 25 and SMRL vulcanizates increase with acid concentration up to maximum value and then decreased. At a similar acid concentration, the SMRL exhibits the highest tensile and tear strengths followed by ENR 25 and ENR 50 compounds.

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