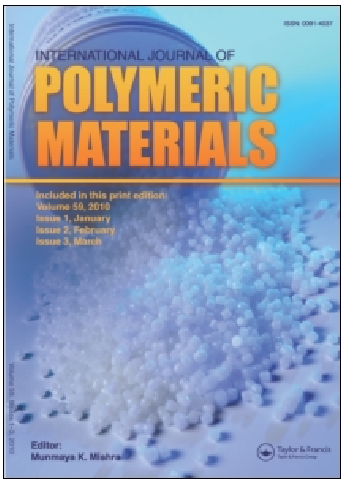

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Concentration Effect of Palm Oil Fatty Acid on Curing Characteristics and Mechanical Properties of Carbon Black Filled Natural Rubber Compounds

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The concentration effect of palm oil fatty acid on curing characteristics and mechanical properties of carbon black filled natural rubber compounds was investigated. Results indicate that maximum torque increases with palm oil fatty acid concentration for all carbon black loadings investigated. Natural rubber compounds with 50 phr of carbon black show highest maximum torque. Scorch time and cure time (t_{90}) also increased with increasing palm oil fatty acid concentration which indicates that this acid has retardation effect on vulcanization. Tensile modulus and hardness increased with increasing acid concentration while tensile and tear strength pass through a maximum.

Keywords: Palm oil fatty acid; curing characteristics; mechanical properties; carbon black; reversion

1. INTRODUCTION

Activators are ingredients used to activate the accelerator and improve its effectiveness. The most widely used activators are zinc oxide, stearic acid, litharge, magnesia, and amines. A cure system consisting of sulphur and organic accelerators usually requires the presence of an adequate amount of zinc oxide and stearic acid to attain good crosslinking efficiency [1]. Studies on the concentration effect of stearic acid on natural rubber was reported by Coran [2, 3]. He found that the specific rate of vulcanization is decreased if the concentration of stearic acid is increased. Poh and Tang [4] reported that scorch time increases with stearic acid content for all the rubbers investigated. Barton and Hart [5] found that modulus values improves as the lauric acid content increases but remains constant above a critical concentration of lauric acid.

Palm oil is predominantly made up of triglycerides. It is sold in the world markets on the basis of a 5% premium/penalty limit for free fatty acids. During the refining process, free fatty acids must be removed. Fatty acids obtained from palm oil processing consist of a mixture of myristic, palmitic, stearic, oleic, linoleic acids, etc. These acids are long straight chain compounds containing an even number of carbon atoms from C_{10} to C_{18}. It is felt that these fatty acids may be used in rubber industry in the same role as the commercial stearic acid. In the study presented here, the concentration effect of palm oil fatty acid on curing characteristics and mechanical properties of carbon black filled natural rubber compounds was investigated. With regard to palm oil fatty acid, ther is no report on the use of these fatty acids in rubber compounds.

2. EXPERIMENTAL

2.1. Materials and Formulations

Table I shows the formulation used in this study. SMR 10 was supplied by Rubber Research Institute of Malaysia (RRIM). Palm oil fatty acid, Palmac 770 was obtained from Acidchem (Malaysia) Bhd., Penang, Malaysia and its specification is shown in Table II. Other ingredients such as zinc oxide, sulphur, antioxidant and accelerator were purchased from Bayer (M) Ltd. while carbon black, N330 was obtained from Malayan Carbon (M) Ltd. All materials were used as supplied and conventional sulphur vulcanization system (CV) was employed.

2.2. Sample Preparation

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 the American Society for Testing and Materials (ASTM), designated D 3184-80. The respective cure times at 150°C as measured by

TABLE I Formulation used to study the effect of palm oil fatty acid in carbon black filled SMR 10 compounds

Materials	*phr*
SMR 10	100
Carbon black (N330)[a]	variable
Zinc oxide	5.0
Sulphur	2.5
MBT[b]	1.2
Flectol H[c]	1.0
Palm Oil Fatty Acid	0.0, 1.0, 3.0, 5.0, 7.0

[a] Used at 15, 30 and 50 phr.
[b] 2-Mercaptobenzothiazole.
[c] Poly-1, 2-dihydro-2, 2, 4-trimethylquinoline.

TABLE II Specification for Palm Oil Fatty Acid (PALMAC 770 - Oleic Acid 80% Min) [6]

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	
Saturated	
$C_{10:0}$ (Caprylic Acid)	6 Max
$C_{12:0}$ (Lauric Acid)	
$C_{14:0}$ (Myristic Acid)	
$C_{16:0}$ (Palmitic Acid)	
$C_{18:0}$ (Stearic Acid)	
Unsaturated	
$C_{18:1}$ (Oleic Acid)	80 Min.
$C_{18:2}$ (Linoleic Acid)	14 Max.

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 Mechanical Properties

The various rubber compounds were compression moulded at 150°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. Reversion

A Monsanto Rheometer, model MDR 2000 was used to test the rubber compound since the rheometer torque is found to be suitable as an indicator of reversion behaviour [7].

Percentage reversion (R) is defined as:

$$R = (T_{\max} - T_t)\,100/(T_{\max} - T_{\min})$$

where $T_{\max}$ = maximum torque, T_t = torque at t minutes and $T_{\min}$ = minimum torque on the rheograph.

2.5. Determination of Crosslink Density

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 was 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 [8] (Equation 1). Physical crosslink density $(2M_c)^{-1}$ was related to volume fraction of rubber in swollen gel by solvent at equilibrium (V_r).

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

where V_r = volume fraction of swollen rubber at equilibrium; X = interaction constant characteristic between rubber sample and toluene (039); 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 was obtained.

3. RESULTS AND DISCUSSION

3.1. Effect on Curing Characteristics

Tables III, IV and V show the values ot t_{90}, scorch time, and maximum torque of palm oil fatty acid in carbon black filled natural rubber compounds at 15, 30 and 50 phr. It can be seen that compared to the control compound (0 phr of palm oil fatty acid), all compounds have higher

TABLE III Cure time (t_{90}), scorch time and maximum torque of 15 phr of carbon black filled natural rubber compounds with palm oil fatty acid as an activator

Palm oil fatty acid (phr)	*0*	*1*	*3*	*5*	*7*
T_{90} (min)	6.54	7.14	7.33	7.54	9.26
Scorch time (min)	1.52	1.55	2.04	2.19	2.32
Maximum torque (dNm)	6.18	6.57	7.34	7.43	7.45

TABLE IV Cure time (t_{90}), scorch time and maximum torque of 30 phr of carbon black filled natural rubber compounds with palm oil fatty acid as an activator

Palm oil fatty acid (phr)	*0*	*1*	*3*	*5*	*7*
T_{90} (min)	6.30	6.55	7.07	8.07	9.11
Scorch time (min)	1.43	1.45	2.01	2.11	2.17
Max torque (dNm)	7.61	8.98	9.41	9.72	10.04

TABLE V Cure time (t_{90}), scorch time and maximum torque of 50 phr of carbon black filled natural rubber compounds with palm oil fatty acid as an activator

Palm oil fatty acid (phr)	*0*	*1*	*3*	*5*	*7*
T_{90} (min)	5.51	6.17	6.22	7.22	8.26
Scorch time (min)	1.25	1.35	1.39	1.41	1.44
Max torque (dNm)	12.25	12.69	12.95	14.89	16.74

maximum torque with increasing amounts of acids used. These tables also show that at similar concentration of palm oil fatty acid, compounds with 50 phr of carbon black show highest maximum torque. Marked increment in the maximum torque with increasing carbon black loadings indicates that the presence of fillers in the rubber matrix has reduced the mobility of the macromolecular chains of the rubber. Figure 1 shows the torque difference, $M_{HR} - M_L$ (Max. torque – Min. torque) of the compounds with increasing concentration of palm oil fatty acid. The increment in the torque difference values shows that palm oil fatty acid has an activating effect to cause more efficient use of sulphur for higher degree of crosslinking. Figure 2 from swelling test result also shows the similar trend as the torque difference values, $M_{HR} - M_L$ with increasing acids concentration. Barton and Hart [5] and Moore and Porter [9] 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 causes faster

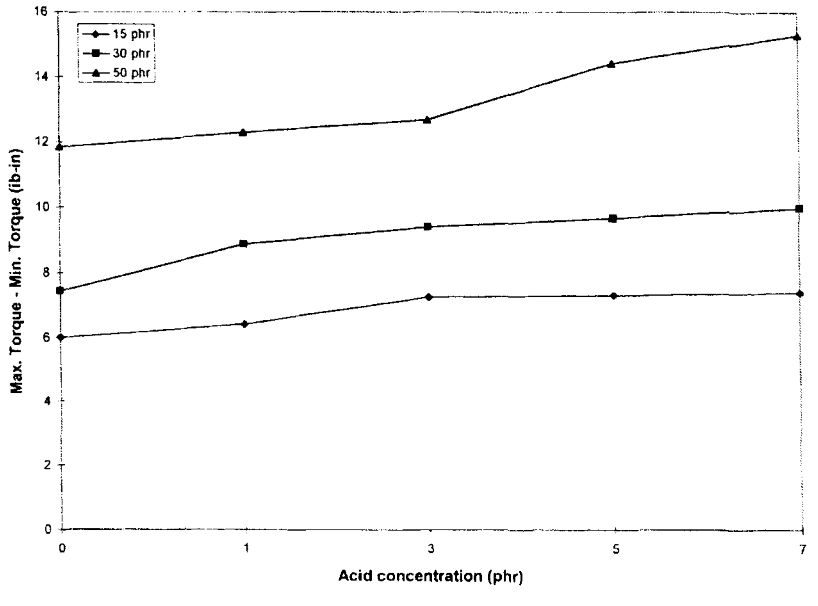

FIGURE 1 The effect of acid concentration on max. torque – min. torque in carbon black filled natural rubber compounds.

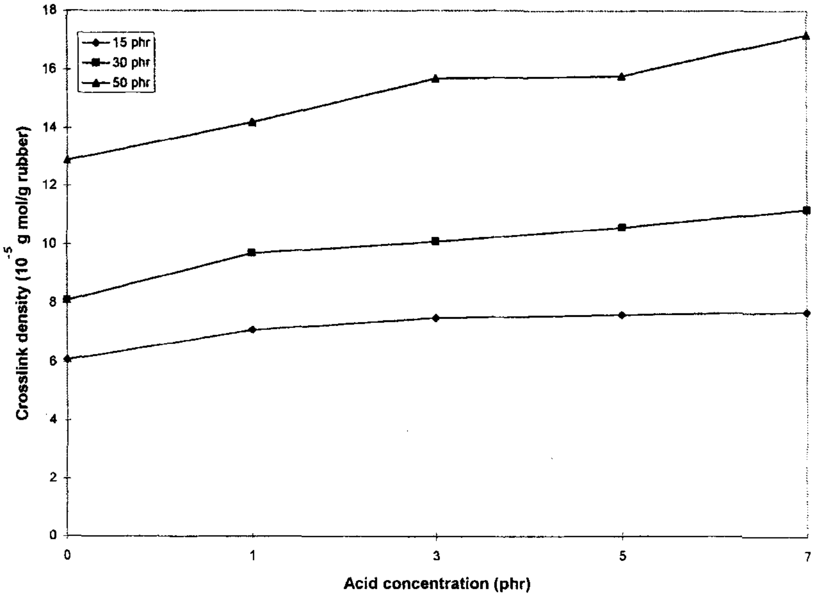

FIGURE 2 The effect of acid concentration on crosslink density in carbon black filled natural rubber compounds.

desulphuration of crosslinking and most of the crosslinking formed was mono and disulphidic [5].

It can be seen from Tables III, IV and V that for the three carbon black concentrations studies, all the data exhibit an increase in t_{90} and scorch time with increasing palm oil fatty acid concentration. This shows that palm oil fatty acid, like other well-known retarders like benzoic acid retard the onset of vulcanization [10]. The data show that palm oil fatty acid slows down the cure rate, thereby retarding the curing process. Poh and Tang [4] also obtained the similar results. According to Coran [2, 3], the increase 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.

For a fixed palm oil fatty acid concentration, the t_{90} and scorch time of the compounds decrease with increasing loading of carbon black. The role of carbon black is to activate the vulcanizing process through the promotion of hydrogen sulfide formation and the rupture of S–N linkage when heated with sulfenamides in rubber, either in the presence or absence of other compounding ingredients [11]. Consequently scorch time decreases with increasing carbon black.

3.2. Effect on Mechanical Properties

Figure 3 shows the effect of palm oil fatty acid on modulus at 300% elongation (M300) of carbon black filled natural compounds at three different carbon black loadings. It can be seen that at 30 phr and 50 phr of carbon black the tensile modulus (M300) increased with increasing acid concentration. However for 15 phr of carbon black, M300 increased up to 3 phr and then decreased slightly with further addition of acid. According to Sloan *et al.* [12], 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. It can be seen from

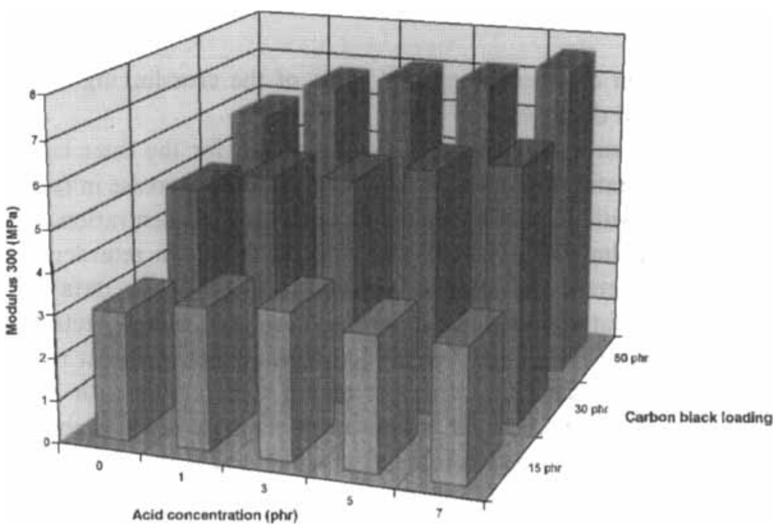

FIGURE 3 Relationship between modulus at 300% elongation (M300) and acid concentration in carbon black filled natural rubber compounds.

Figure 4 that hardness of the compounds increased with increasing acid concentration for all carbon black loadings.

Figure 5 shows the relationship between tensile strength and acid concentration of different carbon black loadings. It can be seen that tensile strength of all compounds increased with acid concentration up to a maximum value and then decreased. Natural rubber compounds with 50 phr of carbon black show the highest tensile strength followed by 30 and 15 phrs. Morrison and Porter [13] reported that increment in the degree of crosslinking may be one of the factors contributing to the enhancement in tensile strength. Actually increment in crosslink density resulted in higher tensile strength at the beginning and then decreased. Table II shows the various types of acid presence in palm oil fatty acid. After the optimum level, some of these acids would act as internal plasticizer which resulted in reduction of tensile strength. Similar trend can be seen in Figure 6 for tear strength. Hamed [14] reported that fracture properties such as tear and tensile strength, pass through a maximum as crosslinking is increased.

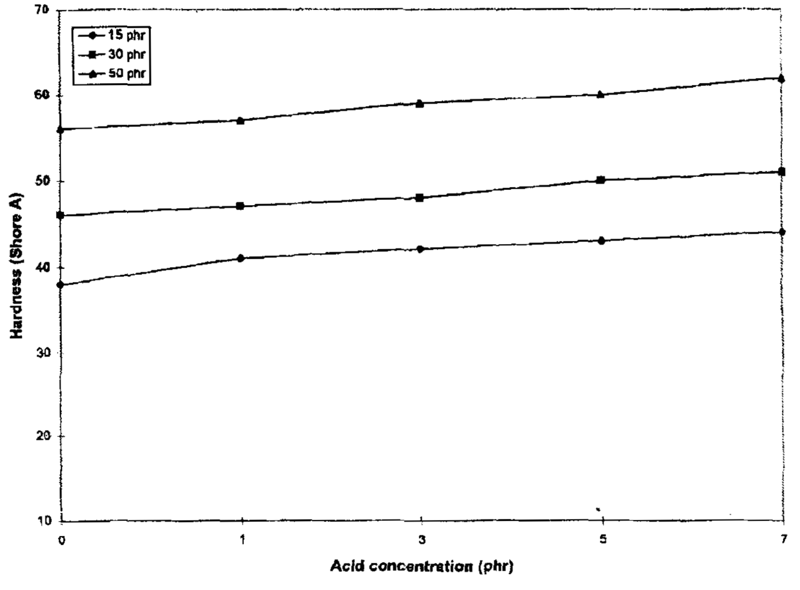

FIGURE 4 The effect of acid concentration on hardness in carbon black filled natural rubber compounds.

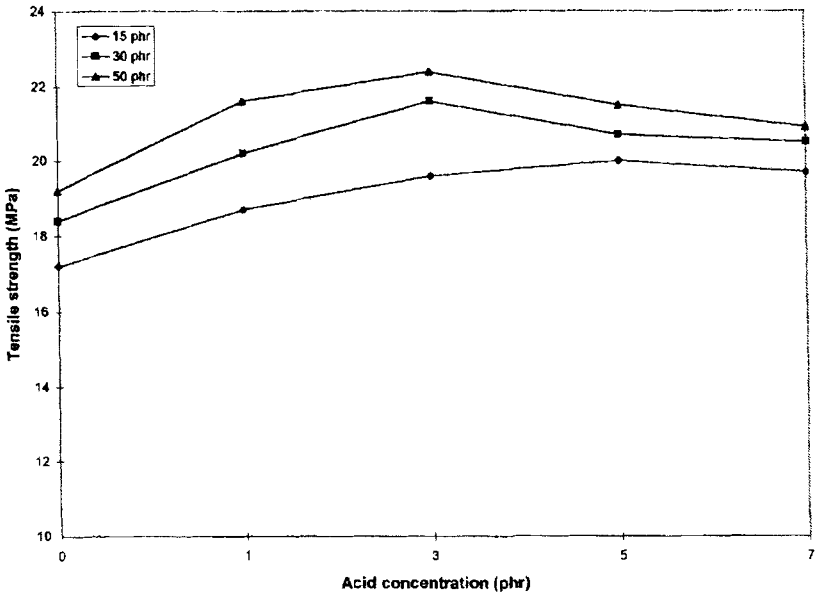

FIGURE 5 Relationship between tensile strength and acid concentration in carbon black filled natural rubber compounds.

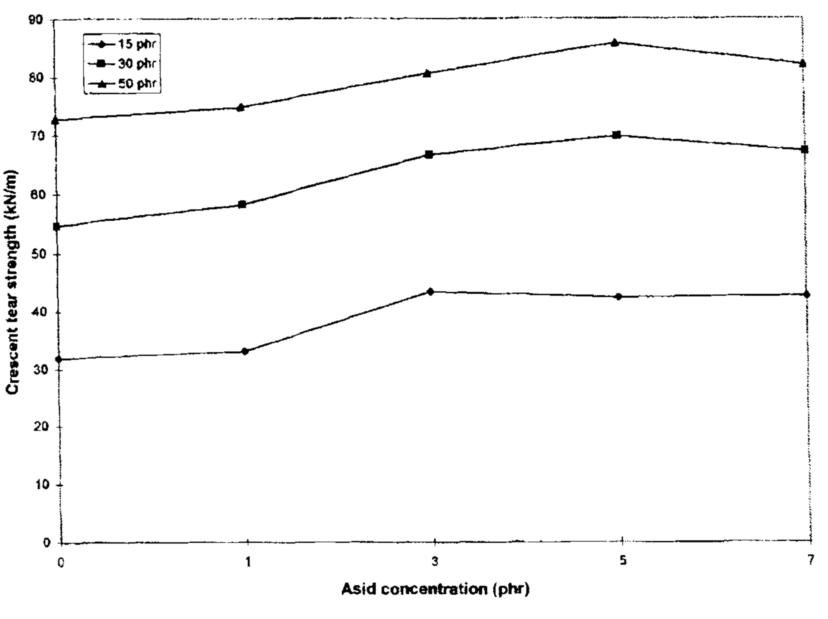

FIGURE 6 The effect of acid concentration on crescent tear strength in carbon black filled natural rubber compounds.

3.3. Reversion

The concentration effect of palm oil fatty acid on the reversion behaviour at 150°C of carbon black filled natural rubber compound at three different carbon black concentrations is shown in Figure 7. For all carbon black concentrations, reversion decreases with an increase in acid concentration indicating the formation of more stable crosslinks, i.e. less polysulphidic type. According to Bristow [15] higher amount of stearic acid in rubber formulations would improve the resistance to reversion. Sloan *et al.* [12] reported the similar result, i.e. the reduction of reversion with increasing concentration of stearic acid. This shows that more stable mono- and disulphidic crosslinks formed as the concentration of acid increased compared to polysulphidic crosslink. Disulphuration process decreased due to less polysulphidic crosslink and led to reduction of reversion.

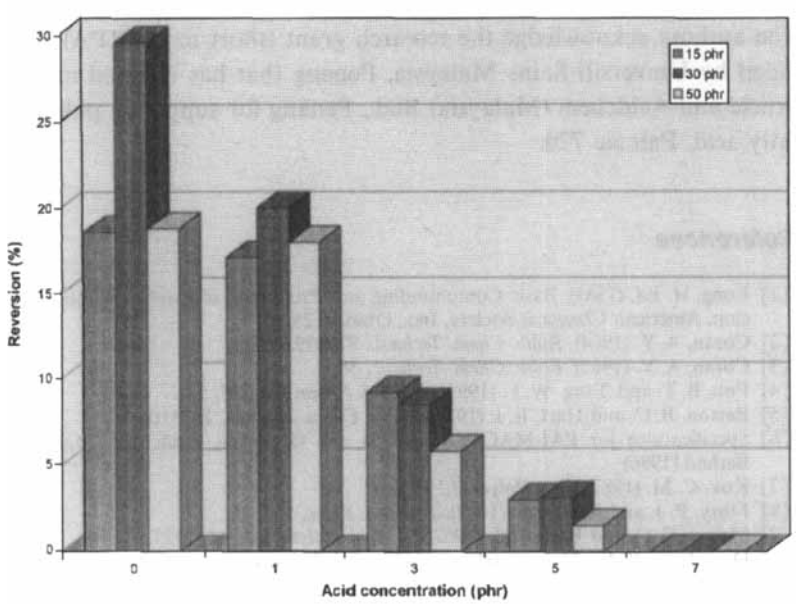

FIGURE 7 Variation of percentage reversion with acid concentration in carbon black filled natural rubber compounds.

CONCLUSION

Based on this study the following conclusions can be drawn:

1. The scorch time and t_{90} increase with concentration of palm oil fatty acid. This show that palm oil fatty acid retards the onset of vulcanization. For a fixed palm oil fatty acid concentration, these properties decrease with increasing loading of carbon black.
2. The difference torque, $M_{HR} - M_L$ increases with concentration of palm oil fatty acid. Results from swelling test show similar trend which indicate that palm oil fatty acid has an activating effect to cause more efficient use of sulphur for higher degree of crosslinking.
3. Compared to control compound, incorporation of palm oil fatty acid give better mechanical properties viz tensile modulus, hardness, tear strength and tensile strength. Compounds with 50 phr of carbon black show the highest mechanical properties followed by 30 and 15 phrs.

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