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The effect of gypsum loadings on the curing characteristics and physico-mechanical properties of natural rubber vulcanisates

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ABSTRACT: The effect of gypsum loading on curing characteristics and physico-mechanical properties of natural rubber vulcanisates were investigated over a range of filler loadings from 0 to 40 phr. Changes with minimum torque (M_L), maximum torque (M_H), scorch time (t_{s2}), 90% cure time (t_{c90}) and curing rate index (CRI), tensile strength, young modulus at 300% elongation (M300), elongation at break, hardness and rebound resilience with the filler loadings were investigated. The results revealed that the values of both the minimum torque and the maximum torque increased with the filler loadings. However, the scorch time was found to decrease and 90% cure time was almost unchanged with increasing filler loadings. The tensile moduli at 300% elongation and hardness increased, whereas, tensile strength, elongation at break and rebound resilience dropped with the addition of filler loadings.

Keywords: *Cure characteristics, Gypsum, Mechanical properties, Natural rubber, Vulcanisation.*

INTRODUCTION

Natural rubber (NR) as one of the important elastomers is widely used in many industries. This is due to its unique property in that it is capable of rapid deformation and recovery and can show crystallization under strain. It also exhibits good hysteretic properties, high tear strength, high tensile strength, and high green strength which are used in certain applications, such as tires, seals, mountings and gaskets [1-7]. One way of achieving improved behavior of NR is the incorporation of a number of additives into the polymer matrix. Additives are materials when incorporated into a rubber base, help to ensure easy processing, reduce cost of final product and improve service life [8-12]. The various types of additives used in the processing of rubber into useful products include, fillers, vulcanizing agents, plasticisers, accelerators, activators, anti-degradants, pigments and etc. Fillers are one of the major additives in natural rubber compounds which can have marked effect on rubber vulcanisate. The ultimate properties like hardness, elasticity and physical parameters depend on the type and loading of the fillers used. It is well established that carbon black is one of the most important reinforcing fillers, especially for the rubber industry. However, carbon black is expensive compared with other fillers which are derived from non-petroleum products. Therefore, numerous research have been carried out to investigate the possibility of replacing all or part of the carbon black with other fillers for producing rubber vulcanisates, because

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of availability of materials, easy processing, low cost and high volume applications. Previous study [10] revealed that using carbon black as reinforcing filler can have an effect on the rheological properties of the rubber vulcanisates. It should be mentioned that considerable research have been carried out on the physico-mechanical propertied of the rubber compounds using various fillers [10-14], there are few published paper on the physico-mechanical of the rubber vulcanisates using gypsum. However, the objective of the present study was to explore the influence of gypsum loading as filler on the physico-mechanical and curing characteristics of the natural rubber vulcanisates.

MATERIALS AND METHODS

Materials

Natural rubber SMR-5 was obtained from Malaysian company and used as received. All other rubber compounding ingredients were of industrial grade and were used without further treatment. Commercial gypsum was collected from a local factory and used as received.

Rubber Compounding

Compounds were prepared by mill mixing on a laboratory size two roll mill at a friction ratio of 1:1.25 as per ASTM D 3184-89. After mixing all the ingredients, the stock was passed number of times through tight nip gap and finally sheeted out a fixed nip gap. The samples were kept for 24 hours for maturation. The base formulation for the preparation of NR compounds is given in Table 1. The samples were designated as C0 to C40. The letter C refers to compound. The number followed the letter indicates the amount of filler in phr. The gum sample (C0) was prepared for comparing properties with those of the filled samples.

Cure Characterisation and Testing

The curing characteristics of the rubber compounds were studied using an Oscillating Disc Rheometer, Alpha ODR 2000 in accordance with the ASTM D 2084-01. About 10 g of rubber compound was placed between a pair of rotating discs which was set at 150°C. The cure time (t_{90}), minimum torque (t_{min}), maximum torque (t_{max}), and scorch time (t_{s2}) which indicates the processing period of the rubber compound at a given temperature before curing refers to the time till two torque above the minimum (t_{min}) were measured from the rheographs. The cure rate index (CRI) and cure time were determined using the expression given below:

$$\text{Cure rate index} = \frac{100}{t_{90} - t_{s2}}$$

$$\text{Curetime} = \frac{90\left(t_{max} - t_{min}\right)}{100} + t_{min}$$

Subsequently, the rubber filled blends were vulcanised up to the optimum cure time at 150°C in an electrically heated hydraulic press. The mouldings were stored in a cool dark place for 24 hours prior to physical testing. Tensile properties of the vulcanisates were measured with a Monsanto Tensile Testing Machine at cross-head speed of 500 mm/min using dumb-bell test specimens according to ASTM D 412-87. The Shore hardness test was carried out according to ASTM D 2240-89 using the Zwick 7206 Hardness Tester on disc shaped samples. The measured value of hardness was obtained at three different points distributed over the test piece. The rebound resilience of the rubber

Table 1. Base formulation of rubber filled compounds.

Ingredient (phr)	C0	C5	C10	C15	C20	C25	C30	C35	C40
Natural rubber (SMR-5)	100	100	100	100	100	100	100	100	100
Zind oxide	3	3	3	3	3	3	3	3	3
Stearic acid	2	2	2	2	2	2	2	2	2
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
MBTD[a]	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Gypsum	0	5	10	15	20	25	30	35	40

[a] Mercaptobezthiazole disulphide.

vulcanisates were determined by Dunlop Tripsometer according to ASTM D 51253-89. In each testing five samples were used and their average values were determined.

RESULTS AND DISCUSSION

Curing Characteristic

The effects of gypsum on the curing characteristics of rubber filled compounds at various filler loadings were investigated and the curing characteristics at 150°C of commercial gypsum filled NR compounds at various filler loadings including the minimum torque (M_L), Maximum torque (M_H), scorch time (t_{s2}), 90% cure time (t_{c90}) and curing rate index (CRI) are shown in Figs. 1 to 5, respectively. As can be seen in Fig. 1 and Fig. 2, when filler loadings increased, the values of both the minimum torque and the maximum torque of the rubber filled compounds increased. This in fact indicated that incorporation of filler from 0 phr to 40 phr into the rubber matrix led to the increased in viscosity and modulus (Table 2) of the rubber compounds.

The scorch time of the filled NR compounds is shown in Fig. 3. The reduction in scorch time is an indication of the enhancement of the cure rate. The reason for the reduction of the scorch time (t_{s2})) is probably due to the longer mixing time required to homogeneously blend higher loadings of gypsum with the rubber. Therefore, a higher shearing force should be applied to the rubbers during the compounding process. This extra force results in more friction, which generates heat. The extra heat accumulated from longer compounding time will cause the compounds to undergo premature curing and thus, result in shorter scorch time.

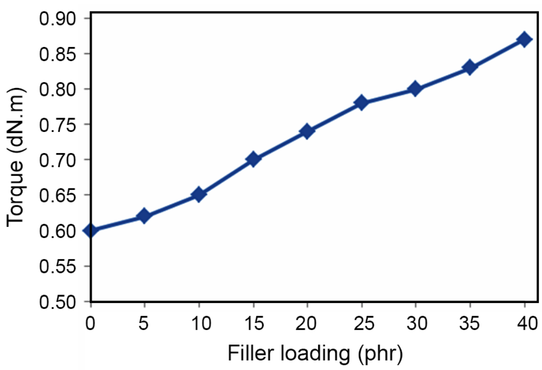

Fig. 1. Minimum torque (M_L) of the filled NR compounds.

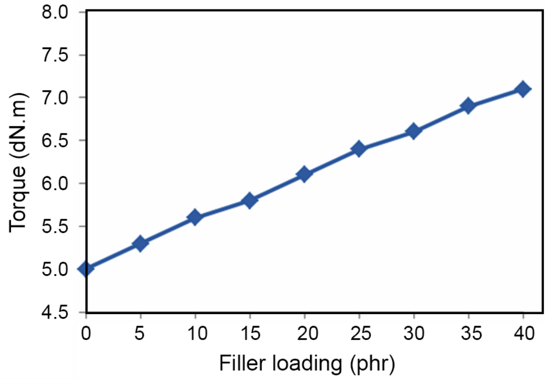

Fig. 2. Maximum torque (M_H) of the filled NR compounds.

The time required for the rubber compounds to reach 90% of the state of cure is shown in Fig. 4, which shows the effect of the filler loadings on the 90% cure time of the filled NR compounds. It can be seen that 90% cure time was almost unchanged by increased amount of filler loadings.

The cure rate index (CRI) of the NR filled compounds which is a measure of the rate of the cure reaction is shown in Fig. 5. It can be seen in Fig. 5 that the cure rate index of the NR filled compounds was affected by increased amount of filler. It was observed that the cure rate index of the NR filled compounds decreased quite significantly compared with unfilled compound.

Mechanical Properties

The effect of filler loadings on the mechanical properties of the rubber filled compounds are shown in Table 2. The results are given as average values.

As shown in Table 2, the tensile moduli of the rubber filled compounds at 300% elongation increased with the addition of filler and increased further as the filler

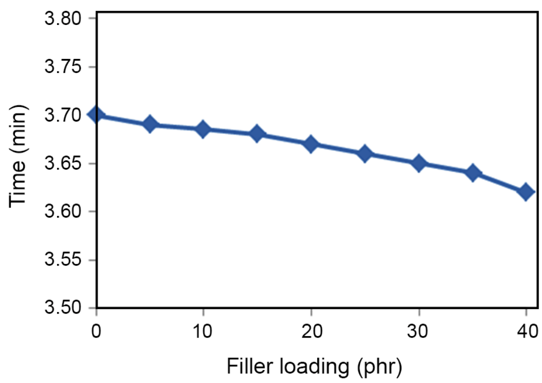

Fig. 3. Scorch time (t_{s2}) of the filled NR compounds.

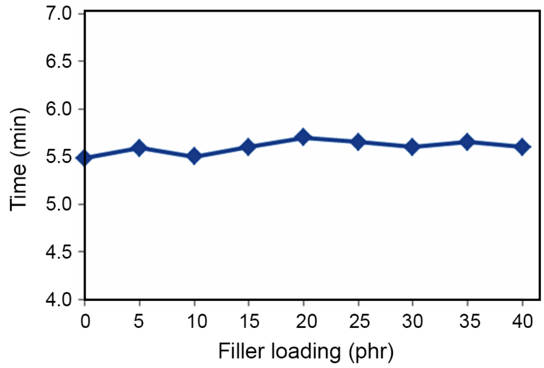

Fig. 4. Cure time (t_{c90}) of the filled NR compounds.

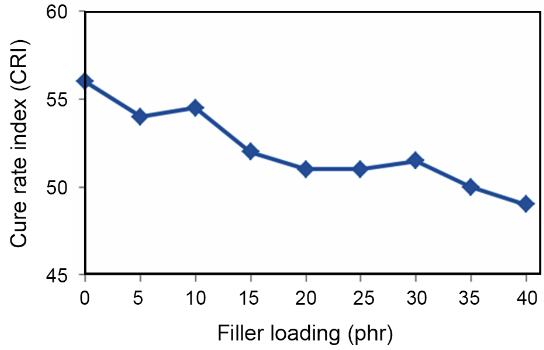

Fig. 5. Cure rate index (CRI) of the filled NR compounds.

loading is increased. This indicated that the addition of filler reduced the elasticity of the rubber chains. The increased in tensile modulus can be associated with the maximum torque (t_{max}) values of the rubber compounds, which increased with filler loading (Table 2). The effect of gypsum loading on the tensile properties of filled rubber compounds were measured with an Instron machine. It can be observed in Table 2 that the tensile strength of the compounds dropped with the addition of gypsum. The highest tensile strength was exhibited by the gum sample (C0) which contained no gypsum due to the ability of the natural rubber chains to undergo strain-induced crystallization compared to other rubber compounds. The elongation at break observed in Table 2, exhibited a gradual decreased with filler loadings. The reduction of the elongation at break is probably due to increasing brittleness of the rubber compounds as a result of the transition from a rubber to a plastic phase with increasing gypsum loadings. The increase in filler loading will tend to restrict the flexibility of the rubber chains and therefore, cause the rubber vulcanisates to fail at a lower elongation [12].

Hardness and Rebound Resilience

The effects of gypsum on the hardness and rebound resilience of the rubber filled compounds at various filler loadings are shown in Table 3. The results are given as average values.

Hardness of the rubber filled compounds increased with increasing gypsum loading as shown in Table 3. It is apparent from Table 3 that the addition of 0 to 40 phr gypsum resulted in increased hardness of the compounds from 30 to 60 Shore A, respectively. This enhancement in hardness of the samples is thought to be due to the fact that as more filler particles are incorporated into the rubber matrix, the elasticity of the rubber chain is reduced, thus, resulting in more rigid compounds. The values obtained for the hardness are in good agreement with the results on modulus (Table 2). On the contrary, it can clearly be seen in Table 3

Table 2. Tensile properties of rubber filled compounds.

Tensile properties	C0	C5	C10	C15	C20	C25	C30	C35	C40
Modulus at 300% elongation (MPa)	1.4	2.0	2.4	3.1	3.5	3.8	4.2	4.5	4.7
Tensile strength (MPa)	18.4	17.6	16.3	15.1	13.2	11.2	10.2	10	9.5
Elongation at break (%)	960	940	900	850	790	740	710	690	660

Table 3. Hardness and rebound resilience of rubber filled compounds.

Property	C0	C5	C10	C15	C20	C25	C30	C35	C40
Hardness (Shore A)	30	33	37	42	48	52	56	57	60
Rebound resilience (%)	58	53	49	45	40	38	32	28	25

that the addition of gypsum from 0 to 40 phr reduced the rebound resilience of the rubber compounds. This is expected because as more filler particles are added to the rubber matrix, flexibility of the rubber chain is reduced, resulting in more rigid vulcanisates.

CONCLUSIONS

In this work cure characteristics and physico-mechanical properties of the natural rubber vulcanisates were investigated. The results indicated that when filler loadings increased, the values of both the minimum torque and the maximum torque of the rubber filled compounds increased. Whereas, the scorch time decreased which is an indication of the enhancement of the cure rate? The 90% cure time was almost unchanged with addition of filler. The tensile moduli of the rubber filled compounds at 300% elongation increased with the addition of filler due to the reduced elasticity of the rubber chains. The tensile strength of the compounds dropped with the addition of gypsum. The highest tensile strength was exhibited by the gum sample which contained no gypsum due to the ability of the natural rubber chains to undergo strain-induced crystallization compared to other rubber compounds (C5 to C40). The elongation at break exhibited a gradual decreased with filler loadings. The reduction of the elongation at break was probably due to increasing brittleness of the rubber compounds as a result of the transition from a rubber to a plastic phase. The addition of 0 to 40 phr gypsum resulted in increased hardness of the compounds from 30 to 60 Shore A, due to the fact that as more filler particles are incorporated into the rubber matrix, the elasticity of the rubber chain is reduced, resulting in more rigid compounds. On the contrary, the addition of gypsum from 0 to 40 phr reduced the rebound resilience because as more filler particles are added the flexibility of the rubber chain is reduced, resulting in more rigid rubber vulcanisates.

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