Effects of epoxidised natural rubbers on cure characteristics and crosslink density of silica-filled natural rubber composite

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Abstract. The effect of two grades of epoxidised natural rubbers (ENR 25 and ENR 50), having 25 and 50 mol of epoxidation, on crosslink density and cure characteristics of silica-filled natural rubber (NR) composites were investigated using a semi-efficient vulcanisation system. The ENRs were incorporated separately into the composites at 5.0, 10.0, 15.0, 20.0 and 25.0 parts per hundred rubber (phr). An investigation was carried out to examine the effects of the ENRs on cure characteristics and crosslink density of the silica-filled NR composites. Results revealed that both ENR 25 and ENR 50 functioned as curatives and compatibilizers. They increased the scorch time, cure time, torque difference and crosslink density. The higher the ENRs loadings; the higher were the scorch, cure times, torque difference and crosslink density. At a similar loading, ENR 50 exhibited a more pronounced curative and compatibilization effects than ENR 25.

1. Introduction

Fillers are rubber additives which are divided into black and non-black fillers. The black filler is carbon black (CB) and non-black fillers are kaolin clay, calcium carbonate (CaCO₃), wollastonite, precipitated silica, talc, barite, mica, precipitated silicates, fumed kaolin and diatomite. Of these, the three most popular in rubber compounding are precipitated silica, kaolin and CaCO₃.

In general, silica and the other non-black fillers are not satisfactory alternatives to CB, because of their inadequate reinforcement levels [1]. The main problem is their surface chemistry which is more polar and hydrated than CB and it is a deficiency which causes them to be difficult to wet, disperse and interact with non-polar rubbers such as natural rubber (NR) [2]. A lot of methods have been performed to improve the reactivity of the non-black fillers with the rubber phases. One of them is the using of a silane-coupling agent. The coupling agent modifies the surface of the filler. The modified polar-filler provides chemically active surfaces that can participate in vulcanisation, providing coupling bonds between silane and both the polar-filler and the rubber phases [3]. Those rubber composites show a significant enhancement in performance compared to their base materials.

The silica, a type of polar-fillers, is easily dispersed in polar rubbers than in NR. Therefore, recipes of the silica-filled NR composites must contain a compatibilizer which provides a greater rubber-filler interaction. In order to solve the deficiency of silica, this work incorporated epoxidised natural rubber (ENR) into silica-filled NR composites. ENR is a polar-rubber and is a product of chemical modification on NR. As the NR is epoxidised, its chemical and physical properties change according
to the extent to which the mole % of modification is introduced [4-5]. The higher the epoxidation degree, the higher is the degree of polarity [6].

This work reports the effects of ENRs addition on cure characteristics and crosslink density of silica-filled NR composites. Two grades of ENRs; ENR 25 and ENR 50 having 25 and 50 mol of epoxidation were used as rubber additives.

2. Experimental
2.1. The materials for research
The raw rubbers (NR, ENR 25, ENR 50) were prepared by RRIM, Malaysia. The mercapto benzothiazolyl disulphide (MBTS), sulfur (S), stearic acid, kaolin, ZnO and antioxidant (IPPD) were obtained from the Bayer Company, Malaysia. The precipitated silica was supplied by Bayer Co. (M) Sdn. Bhd., Petaling Jaya, Selangor, Malaysia

2.2. The composites preparation
The semi-efficient vulcanisation was utilized for composite preparation. The composite preparation procedure was executed according to the ASTM (D3184 – 80). The composite preparation was done on the two roll mill with XK-160 Model. Table 1 presents the recipe of NR composite with different ENRs concentrations.

| Materials       | Composition (phr) |
|-----------------|-------------------|
| NR              | 100               |
| S               | 1.5               |
| ZnO             | 5                 |
| MBTS            | 1.5               |
| IPPD            | 2                 |
| Stearic acid    | 2                 |
| Precipitated silica | 30          |
| ENRs*           | 0; 5; 10; 15; 20 and 25 |

*ENR 25 or ENR 50

2.3. The curing
Scorch time, cure time, maximum and minimum torques and also torque difference of NR composites with and with no ENRs were determined utilising an MDR2000 (Monsanto Moving Die Rheometer) ASTM, D2084-11. The composite sample was tested at 150 °C.

2.4. Crosslinking density determination
The crosslinking density was determined using toluene according to ASTM D471-12a. The (30mm × 5mm × 2mm) sized of composites were weighed on a balance and swollen them inside toluene for 72 hrs (ambient temperature). The composites were taken out from solution and cleaned remained toluene from the surfaces of composites and their weights were marked. The composites were dried inside an oven (70 °C) for constant weights were reached. The data can be used for calculation the weight of molecular between 2 crosslinking, \( M_c \), based on Equations 1 and 2 [7-8].

\[
M_c = \frac{-\rho_r V_r \sqrt[3]{V_r}}{\ln(1 + V_r + \chi V_r^2)}
\]

\[
V_r = \frac{1}{1 + Q_m}
\]
in which \( \rho_r \), rubber density (\( \rho_r \) of NR is 0.92 g.cm\(^{-3} \)), \( V_s \), toluene molar volume (\( V_s \) is 106.4 cm\(^3\).mol\(^{-1}\)), \( V_r \), NR volume fraction in swollen composite, \( Q_m \), composite additional weights in toluene, \( \chi \), parameter of interaction of NR network - toluene (\( \chi \) for NR is 0.393), and the crosslinking density is in \( V_c \) (mol per cubic centimetre).

\[
V_c = \frac{1}{2M_c}
\]  

(3)

3. Results and Discussion
3.1. The cure characteristics

The effects of ENRs additions on cure characteristics of the silica-filled NR composites are shown in Figs. 1-5. From Fig. 1, the scorch times (\( t_s \)) of silica-filled NR composites with ENRs were higher than those of without ENRs (control composite). It was due to the function of both ENRs as curative additives which facilitated the starting point of vulcanisation. Curative additives affect an important role in determining the cure characteristics of rubber composites [9]. They affect the rate and nature of the vulcanisation.

![Figure 1. The effect of ENRs loading on scorch time of silica-filled NR composites.](image)

As shown in Figure 2, the addition of each 5.0 phr of ENR 25 or ENR 50 into the control composite increased the cure time. It indicated that ENRs functioned as curative additives which affected the cure rate. The epoxide groups might interact with silanol groups of silica and consequent to a higher cure time.
As shown in Figs. 1 and 2, the higher the ENRs loading, the higher were the scorch and cure times. It was due to a more amount of epoxide groups in silica-filled NR composites. At a similar ENR loading, the scorch and cure times of ENR 50 were longer than those of ENR 25. It was simply due to the degree of epoxidation of ENRs; ENR 50 has more epoxide groups than ENR 25.

As shown in Figure 3, the addition of each 5.0 phr of ENR 25 or ENR 50 decreased the minimum torque; however, the minimum torque was constant with further increases of ENRs loadings. The minimum torque relates to filler-filler inter-agglomeration [10] and it is used to measure the relative viscosity of a rubber composite [1]. The lower the value, the weaker the filler-filler interaction is; resulting in a lower viscosity of a rubber composite. Fundamentally, the incorporation of ENRs into the filled NR composites, its effect was the same as an increase in total rubber content of the filled NR composites.
composite. It increased the concentration of rubber phases which decreased in viscosity of the filled 
NR composites. As a consequent, the processability or degree of silica dispersion was improved.

As shown in Figure 4, the additions of 5.0 phr of each type of ENRs increased the maximum 
torque. The maximum torque corresponds with measurement of stock modulus which was increased in 
this case. It was attributed to the nature of rubber-filler interaction including intercalation and exfoliation [11]. The increases in maximum torque were more pronounced whenever the ENRs 
loadings were further increased up to 25.0 phr. The intercalation, exfoliation and rubber-filler 
interaction were further increased also. In this case, the ENRs might be considered as compatibilizers 
in the silica-filled NR composites.

Figure 4. The effect of ENRs loading on maximum torque of the silica-filled NR composites.

Figure 5 shows the effect of ENRs on the torque difference \( (M_H-M_L) \) of the silica-filled NR 
composites. The torque difference indicates the total crosslink density of a rubber composite [11-15]. The greater the torque difference, the higher is the total crosslink density. Generally, the total crosslink 
density of a rubber composite contains sulphide and physical crosslinks [16-19]. ENRs can undergo 
acetic acid catalyst ring-opening reactions via ether crosslinks during curing, resulting in an increase in 
crosslink density [4]. Therefore, the total crosslink density of the silica-filled NR composites might 
contain sulphide, ether and physical crosslinks due to the presence of ENR.

As shown in Fig. 5, the addition of 5.0 phr of ENR 25 or ENR 50 increased the torque difference 
\( (M_H-M_L) \) of the control composite. The higher the ENRs loadings, the higher were the torque 
differences. It was due to the functions of ENRs not only as curative ingredients but also as 
compatibilizers. During curing, the curatives and ENRs enhanced the rate and state/degree of the 
formations of sulphide and ether crosslinks. Simultaneously, they reduced filler-filler agglomeration 
and improved rubber-filler interaction, respectively. The rubber-filler interaction is defined as physical 
crosslinks [17].

At a similar ENR loading, the torque differences of ENR 50 were higher than those of ENR 25. 
Again, it showed that the degree of epoxidation has played an important role in the curing process of 
the filled NR composites. ENR 50 systems with more epoxide groups produced a higher degree of 
additional ether crosslinks than ENR 25 systems.
Figure 5. The effect of ENRs loading on torque difference of the silica-filled NR composites.

3.2. The crosslink density

The effect of ENRs on the total crosslink density of the silica-filled NR composites is shown in Fig. 6. The total crosslink density was determined by the Flory-Rehner approach [Eq. (1)]. The additions of 5.0 phr of each ENRs into the silica-filled NR composites increased the total crosslink density and further increases the ENRs loadings increased the total crosslink density. This observation is in line with the result of the torque difference as presented in Fig. 5. It surely confirms that torque difference indicates the degree of crosslink density of the filled NR composites.

At a similar ENR loading, the total crosslink density of ENR 50 systems was higher than that of ENR 25 systems. It was attributed a higher degree of sulphide, ether and physical crosslinks altogether of ENR 50 systems compared to ENR 25 systems.

Figure 6. The effect of ENRs loading on crosslink density of the silica-filled NR composites.
4. Conclusions

Epoxidised natural rubbers were curatives additives in silica-filled natural rubber composites. They increased the scorch time, cure times, torque difference of silica-filled natural rubber composites. Epoxidised natural rubbers also were compatibilizers. They improved the filler dispersion, rubber-filler interaction and crosslink density of silica-filled natural rubber composites. The higher the loading of epoxidised natural rubber in the silica-filled natural rubber composites; the more pronounced were the curative and compatibilization effects.

At a similar loading, the curative and compatibilization effects of epoxidised natural rubber with 25 mol epoxidation were higher than those of epoxidised natural rubber with 25 mol epoxidation.

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