Effect of epoxidised natural rubbers on curing characteristics of kaolin-filled natural rubber composites

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Abstract. Effects of 2 types of epoxidised natural rubbers (ENR 25, ENR 50), with twenty-five and fifty moles of epoxidation, on crosslinking density and cure characteristics of natural rubber (NR) composites, which were filled by kaolin filler, were investigated using a semi efficient vulcanisation system. The ENRs were added separately into composites at 5.0, 10.0, 15.0, 20.0 and 25.0 parts per hundred rubber. An observation was conducted to investigate the effects of the ENRs on curing and crosslinking density of the kaolin-filled NR composites. Results revealed that both ENR 25 and ENR 50 functioned as curatives and compatibilizers. They decreased both cure and scorch times and minimum torque but increased difference of torque and crosslinking density. The higher ENRs loadings; the lower were the cure time and scorch time, the higher were the torque difference and crosslinking density. At a similar addition, ENR 50 exhibited a more pronounced curative and compatibilization effects than ENR 25.

1. Introduction

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

Generally, kaolin and others non black fillers are inadequate reinforcement levels to CB [1]. The root of the problem is the polarity of them compared to CB and causing them hard to be wetted by natural rubber (NR) - a non polar rubber [2]. A lot of efforts have been performed to enhance reactivity of non blacks with phases of NR. One popular effort was the application of silane coupling agents. It modified chemically polar filler and hence, the modified filler offers some active surfaces which participated in the cure, serving silane and both filler and NR coupling bonds [3]. Those NR mixtures show an excellence performance compared to their basic materials.

Kaolin is a polar filler and it is more readily dispersed inside polar rubbers compared to NR. As a consequence, recipes of NR composites with kaolin should have a compatibilizer that provides a relatively stronger rubber to filler interaction. In solving the problem of poor degree of kaolin dispersion, this research-work used epoxidised natural rubber (ENR) as a compatibilizing agent when
NR was compounded with kaolin. ENR is a polar-rubber and is a product of chemical modification on NR. Beyond epoxidation, the physical and chemical properties of the ENR is changed regarding to extension of mole percentage of introduced-modification [4-5]. A higher epoxidation degree serves a higher in the degree of polarity of ENR [6].

This research-work reports the influences of ENRs addition on curing and crosslinking density of kaolin-filled NR composites. The ENR 25 and ENR 50 with twenty-five and fifty moles of epoxidation were utilised as compatibilizers.

2. Experimental

2.1. The materials for research

The raw rubbers NR, ENRs 50 and 25 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.

2.2. The composites preparation

The semi-efficient vulcanisation was performed 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 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              |
| Kaolin    | 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].

\[
M_c = \frac{- \rho_f V_f V_r^{1/3}}{\ln(1 - V_f) + V_f + \chi V_r^2}
\]
\[ V_r = \frac{1}{1 + Q_m} \]  \hspace{1cm} (2)

in which \( \rho_r \), rubber density (\( \rho_r \) of NR is 0.92 g.cm\(^{-3} \)), \( V_t \), toluene molar volume (\( V_t \) 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).

\[ V_c = \frac{1}{2M_c} \]  \hspace{1cm} (3)

3. Results and Discussion

3.1. The cure

The ENRs effects on cure of the kaolin-filled NR composites are shown in Figures 1-5. Fig. 1 shows that scorch times of the composites with ENRs were lower than those of with no ENRs. It was due to the function of both ENRs as curative additives which facilitated the starting point of vulcanisation. They affect a principal role in determining curing characteristics of composites [11]. They influence both rate and nature of curing reaction.

As visualized in Fig. 2, the 5.0 phr addition of each ENR into control composite reduced cure time. It was a curing enhancement. Again, it indicated that ENRs functioned as curative additives which improved the cure rate. The curing enhancement was due to epoxide groups of ENRs which affected an important impact in the curing of kaolin-filled NR composites. They activated the adjacent double bonds of the rubbers and consequent to a faster cure rate [12].

As visualized in Figs. 1 and 2, a higher ENRs loading caused a lower in scorch times and cure times. It was attributed to a more epoxide groups in the composites. At a similar ENR addition, cure times and scorch times of ENR 50 were shorter compared to ENR 25. It was clearly due to the degree of epoxidation of ENRs; ENR 25 has fewer epoxide groups than ENR 50.
Figure 2. Effect of ENRs addition on cure time of kaolin-filled NR composites

As visualized in Fig. 3, the 5.0 phr addition of each ENR reduced minimum torque; however, minimum torque was constant with further increases of ENRs loadings. Minimum torque relates to filler to filler interaction [13]. It is applied to determine viscosity of a composite relatively [1]. The minimum torque with a lower value means a weaker such interaction; causing in a lower viscosity of a rubber composite. Fundamentally, the incorporation of ENRs into the composites, their effects were the same as an increase in total rubber content of the filled NR composite. It increased the concentration of rubber phases which decreased in viscosity of filled NR composites. As a consequent, the processability or degree of kaolin dispersion was improved.

Figure 3. Effect of ENRs addition on minimum torque of kaolin-filled NR composites

From Fig. 4, the addition of five phr of each ENR slightly enhanced maximum torque. The maximum torque corresponds with measurement of modulus of stock which was enhanced. It was attributed to the type of rubber to filler interaction includes exfoliation and intercalation [14]. The
enhancement in maximum torque was more significant when ENRs concentrations were further enhanced (up to twenty five phr). The intercalation, exfoliation and also rubber to filler interaction were further increased also. In this case, the ENRs might be considered as compatibilizers in the kaolin-filled NR composites.

Fig. 4 visualizes the influences of ENRs on the torque difference ($M_{H}$-$M_{L}$) of the kaolin-filled NR composites. The value of torque difference indicates composites total crosslinking density [14-16]. A greater value of torque difference means a higher total crosslinking density. Generally, total crosslinking density of a rubber composite contains sulphide and physical crosslinking [17-18]. ENRs can undergo reactions of acid catalyst ring-opening through ether crosslinking during curing, resulting in an increase in crosslinking density [4]. Therefore, the total crosslinking density of the composites might contain sulphide, ether and physical crosslinking due to the presence of ENR.

As visualized in Fig. 5, the incorporation of five phr of ENR 25 or ENR 50 enhanced torque difference of control. The higher the ENRs loadings, the higher were the torque differences. It was attributed 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 crosslinking. Simultaneously, they reduced filler-filler agglomeration and improved filler to rubber interaction, respectively. The filler to rubber interaction is considered as physical crosslinking [18, 22].

At a similar ENR addition, torque differences of ENR 50 were higher than those of ENR 25. Again, it showed that degree of epoxidation has played a principal role in curing reaction of filled NR composites. ENR 25 systems with fewer epoxide groups produced a lower degree of additional ether crosslinking than ENR 50 systems.
3.2. The crosslinking density

The influence of ENRs on total crosslinking density of the composites is visualised in Fig. 6. The composites total crosslinking density can be calculated using Flory-Rehner equations [Eqs. (1 and 2)]. The five phr incorporation of each ENR enhanced the total crosslinking density and further increases ENRs loadings increased total crosslinking density. This examination is in agree with torque difference as visualized in Fig. 5. Clearly, torque difference corresponds with degree of crosslinking density.

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

4. Conclusions
1. Epoxidised natural rubbers were curatives additives in kaolin-filled natural rubber composites. They reduced cure times and scorch times but enhanced maximum torque and torque difference of kaolin-filled natural rubber composites.

2. Epoxidised natural rubbers also were compatibilizers. They enhanced the degree of kaolin dispersion, filler to rubber interaction and crosslinking density of kaolin-filled natural rubber composites.

3. The higher the epoxidised natural rubber concentration; the more pronounced were curative and compatibilization effects.

4. At a similar loading, the curative and compatibilization effects of epoxidised natural rubber with 50 moles epoxidation were higher than those of epoxidised natural rubber with 25 moles epoxidation.

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