Malaysian Journal of Analytical Sciences, Vol 22 No 6 (2018): 1014 - 1022
DOI: https://doi.org/10.17576/mjas-2018-2206-11

MALAYSIAN JOURNAL OF ANALYTICAL SCIENCES
Published by The Malaysian Analytical Sciences Society
ISSN
1394 - 2506

EFFECT OF EPOXIDISED NATURAL RUBBERS ON CALCIUM CARBONATE-FILLED NATURAL RUBBER COMPOUNDS

(Kesan Getah Asli Terepoksida Terhadap Sebatian Getah Asli Terisi Kalsium Karbonat)

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Received: 27 July 2017; Accepted: 28 April 2018

Abstract

By using a semi-efficient vulcanisation system, two grades of epoxidised natural rubbers (ENR 25 and ENR 50) were incorporated separately into calcium carbonate ($CaCO_3$) filled natural rubber (NR) compounds at 5.0, 10.0, 15.0, 20.0 and 25.0 phr. An investigation was carried out to examine the effects of the ENRs on cure characteristics, rubber - filler interaction and crosslink density of the $CaCO_3$ filled NR compounds. Results revealed that both ENR 25 and ENR 50 functioned as curatives and compatibilizers. They decreased the scorch time, cure time and minimum torque; increased torque difference, crosslink density and degree of rubber - filler interaction. The higher the ENRs loadings; the lower were the scorch and cure times and the higher were the torque difference, crosslink density and degree of rubber - filler interaction. At a similar loading, ENR 50 exhibited a more pronounced curative and compatibilization effects than ENR 25.

Keywords: epoxidised natural rubber, calcium carbonate, cure characteristics, natural rubber, rubber - filler interaction

Abstrak

Dua gred getah asli terepoksida (ENR 25 dan ENR 50) dimasukkan secara berasingan ke dalam sebatian getah asli terisi kalsium karbonat pada 5.0, 10.0, 15.0, 20.0 dan 25.0 phr dengan menggunakan kaedah pemvulkanan separa cekap (semi-EV). Kajian terhadap sebatian untuk mengkaji kesan ENR terhadap ciri-ciri pematangan, interaksi getah-pengisi dan ketumpatan sambung-silang telah dijalankan. Hasil kajian menunjukkan kedua-dua gred ENR berfungsi sebagai kuratif dan pengserasi. ENR 25 dan ENR 50 memberikan kesan penurunan terhadap masa pembakaran, masa pematangan dan tork minima; peningkatan perbezaan tork, ketumpatan sambung-silang dan darjah interaksi pengisi-getah. Semakin meningkat jumlah kedua-dua ENR, semakin rendah nilai masa pembakaran dan pematangan dan semakin tinggi nilai perbezaan tork, ketumpatan sambung-silang dan darjah interaksi pengisi-getah. Pada nilai muatan yang sama, ENR 50 menunjukkan kesan yang lebih baik sebagai kuratif dan pengserasi berbanding ENR 25.

Kata kunci: getah asli terepoksida, kalsium karbonat, ciri-ciri pematangan, getah asli, interaksi getah-pengisi

Introduction

In rubber science and technology, fillers can be divided into black and non-black fillers. The black filler is carbon black (CB), and non-black fillers are calcium carbonate ($CaCO_3$), kaolin clay, precipitated silica, talc, barite, wollastonite, mica, precipitated silicates, fumed kaolin and diatomite. Of these, the three most widely utilised, by volume and by functionality, are $CaCO_3$, precipitated silica and kaolin.

Due to their inadequate reinforcement levels, $CaCO_3$ and the other non-black fillers are not satisfactory alternatives to CB when it comes to numerous applications [1]. The fundamental problem is their surface chemistry which is more polar and hydrated than CB. It can be considered as a deficiency which causes them to be difficult to wet, disperse and interact with non-polar rubbers such as natural rubber (NR) and styrene butadiene rubber [2]. Numerous methods have been carried on to improve the reactivity of the non-black fillers with the rubber phases. One of them is the utilising 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 products/vulcanisates show a significant improvement in performance compared to their base materials.

The $CaCO_3$, a type of polar-fillers, can be easily dispersed in polar rubbers than in non-polar ones, like NR. Therefore, recipes or formulations of the $CaCO_3$ – NR system must contain a compatibilizer which promotes a greater rubber – filler interaction. In order to overcome the deficiency of $CaCO_3$, this research work incorporates epoxidised natural rubber (ENR) into $CaCO_3$ filled NR compounds. 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].

In this work, the effects of the incorporation of ENRs on cure characteristics, rubber - filler interaction and crosslink density of $CaCO_3$ filled NR compounds were investigated. Two grades of ENRs; ENR 25 and ENR 50 having 25 and 50 mol of epoxidation were utilized as additive ingredients.

Materials and Methods

Materials

NR grade SMR-L was obtained from Guthrie (M) Sdn. Bhd., Seremban, Malaysia. ENR 25 and ENR 50 were supplied by the Rubber Research Institute Malaysia (RRIM). Other compounding ingredients such as sulphur (S), zinc oxide (ZnO), stearic acid, N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD), Mercapto benzothiazolyl disulphide (MBTS) and $CaCO_3$ were supplied by Bayer Co. (M) Sdn. Bhd., Petaling Jaya, Selangor, Malaysia. All materials were used as supplied. The molecular structure of ENR is presented in Figure 1.

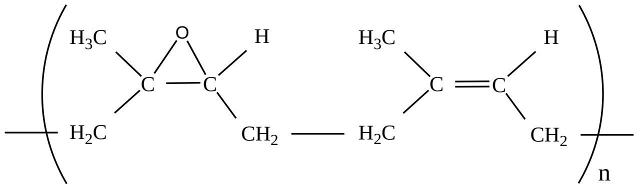

Figure 1. The molecular structure of epoxidized natural rubber.

Compounding

A semi-efficient vulcanisation system was used for the rubber compounding. The compounding procedure was done in accordance with the American Society for Testing and Material (ASTM) – Designation D 3184 – 80. The compounding was performed on a two-roll mill (Model XK-160). Table 1 displays the compound formulation of $CaCO_3$ filled NR compounds with various ENRs loading.

Table 1. The composition of the $CaCO_3$ filled NR compounds

Ingrediants	**Content (phr)**[a]
SMR-L	100.0
ZnO	5.0
Stearic acid	2.0
IPPD	2.0
MBTS	1.5
S	1.5
$CaCO_3$	30.0
ENRs[b]	0.0; 5.0; 10.0; 15.0; 20.0 and 25.0

[a] *parts per hundred part of SMR-L,* [b] *ENR 25 or ENR 50*

Cure characteristics

The cure characteristics of the $CaCO_3$ filled NR compounds with and without ENRs were obtained using a Monsanto Moving Die Rheometer (MDR 2000) which was employed to determine the scorch time (ts_2), cure time (t_{90}), minimum torque (M_L), maximum torque (M_H) and torque difference (M_H—M_L) according to ASTM D2084-11. Samples of the respective compounds were tested at 150 °C.

Measurement of Crosslink Density

Swelling tests on the $CaCO_3$ filled NR vulcanisates were performed in toluene in accordance with ASTM D471-12a. The cured test pieces (30 mm × 5 mm × 2 mm) were weighed using an electric balance and swollen in toluene until equilibrium, which took 72 hours at room temperature. The samples were taken out from the liquid, the toluene was removed from the sample surfaces and the weight was determined. The samples were then dried in the oven at 70°C until constant weights were obtained. The swelling results were used to calculate the molecular weight between two crosslinks (M_c) by applying the Flory-Rehner equation [7-8].

$$M_c = \frac{-\rho_r V_s V_r^{1/3}}{\ln(1-V_r) + V_r + \chi V_r^2} \tag{1}$$

$$V_r = \frac{1}{1+Q_m} \tag{2}$$

where ρ_r is the rubber density (ρ_r of SMR-L = 0.92 g/cm^3), V_s is the molar volume of the toluene (V_s = 106.4 cm^3/mol), V_r is the volume fraction of the rubber in the swollen specimen, Q_m is the weight increase of the vulcanisate in toluene and χ is the interaction parameter of the rubber network−solvent (χ of SMR-L = 0.393). The crosslink density is given in equation 3:

$$V_c = \frac{1}{2M_c} \tag{3}$$

where V_c is the crosslink density in mol per cubic centimetre.

Measurement of rubber - filler interaction

The rubber - filler interaction was determined by swelling the cured $CaCO_3$ filled NR compounds with and without ENRs in toluene, according to ISO 1817. Test pieces with dimensions of (30mm x 5mm x 2mm) were prepared from the moulded sheets. The initial weights were recorded prior to testing. The test pieces were then immersed in toluene and conditioned at room temperature in a dark environment for 72 hours. After the conditioning period, the weights of the swollen test pieces were recorded. The swollen test pieces were then dried in the oven at 70 °C for 15 minutes and were allowed to cool at room temperature for another 15 minutes before the final weights were recorded. The Lorenz and Park's equation [9-10] was applied in this study. The swelling index was calculated according to equation 4.

$$Qf/Qg = ae^{-z} + b \qquad (4)$$

where the subscripts f and g referred to filled and gum vulcanisates, respectively; z was the ratio by weight of filler to hydrocarbon rubber in the vulcanizate; while a and b were constants. The lower the Qf/Qg value, the greater the rubber - filler interaction is [10]. In this study, the weight of the toluene uptake per gram of hydrocarbon rubber (Q) was calculated based on equation 5.

$$Q = [\text{Swollen} - \text{Dried weight}]/[\text{Initial weight} \times 100/\text{Formula weight}] \qquad (5)$$

Results and Discussion

The cure characteristics

The effects of ENRs on the cure characteristics of the $CaCO_3$ filled NR compounds are shown in Figures 2-6. The cure characteristics were measured at 150 ^oC including scorch time, cure time, minimum torque, maximum torque and torque differences. As shown in Figure 2, the scorch times (ts_2) of $CaCO_3$ filled NR compounds with ENRs were lower than those of without ENRs (control compounds). In this case, ENRs functioned as curative ingredients which facilitated the starting point of vulcanisation or curing reaction. Curative ingredients play an important role in determining the cure characteristics of rubber compounds [11]. They affect the rate and nature of the curing process.

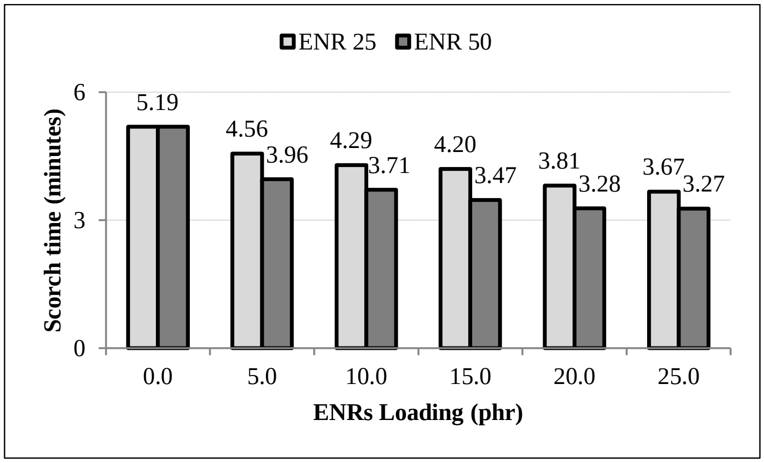

Figure 2. The effect of ENRs loading on scorch time (ts_2) of the $CaCO_3$ filled NR compounds

Figure 3 shows that the addition of each 5.0 phr of ENR 25 or ENR 50 into the control compounds decreased the cure time (t_{90}). A decreasing cure time means an enhancement in cure rate. Again, this indicates that ENRs functioned as curative ingredients which enhanced the cure rate. The cure enhancement was attributed to the epoxide groups of ENRs which played an important role in the curing of the $CaCO_3$ filled NR compounds. The epoxide groups activated the adjacent double bonds of the rubbers and hence, a faster cure rate was observed [12].

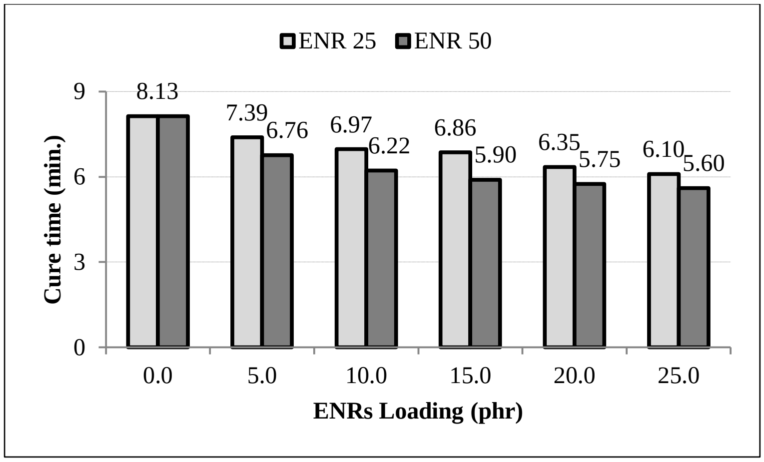

Figure 3. The effect of ENRs loading on cure time (t_{90}) of the $CaCO_3$ filled NR compounds

It can be seen from Figures 2 and 3 that the higher the ENRs loading, the lower were the scorch and cure times. It was attributed to the more and more epoxide groups presented in $CaCO_3$ filled NR compounds. At a similar ENR loading, the scorch and cure times of ENR 50 were shorter than those of ENR 25. It was simply attributed to the degree of epoxidation of ENRs; ENR 50 has more epoxide groups than ENR 25.

Figure 4 shows that the addition of each 5.0 phr of ENR 25 or ENR 50 into the control compounds decreased the minimum torque; however, the minimum torque was constant with further increases of ENRs loadings. The minimum torque indicates qualitatively the filler-filler inter agglomeration [13] and it can also be used to measure the relative viscosity of a rubber compound [1]. The lower the value, the weaker the filler - filler interaction is; resulting in a lower viscosity of a rubber compound. Actually, the incorporation of ENRs into the filled NR compounds, its effect was the same as an increase in total rubber content of the filled NR compound. This affected in an increase in the concentration of rubber phases and a decrease in viscosity of the filled NR compounds. As a consequent, the processability or degree of $CaCO_3$ or filler dispersion in the rubbers systems was improved.

The same minimum torque observed at 5 – 25 phr ENR loading for both NR25 and ENR50 was due to the almost equal of viscosity of both ENRs. ENRs are less viscous than NR and, the viscosity of ENR 25 is quite equal to the viscosity of ENR 50.

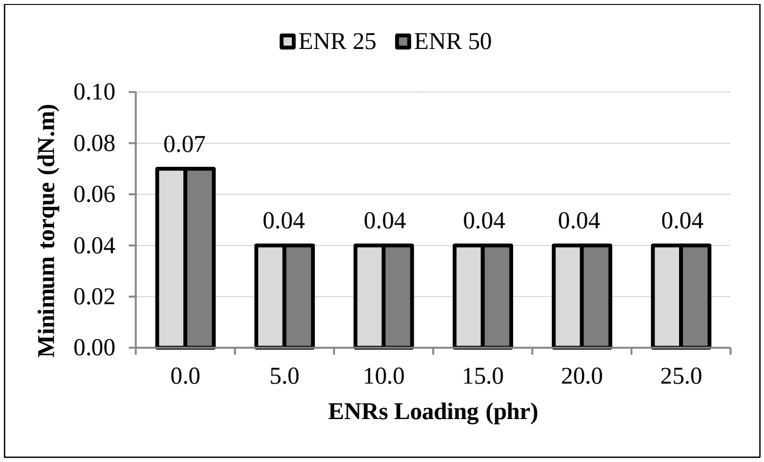

Figure 4. The effect of ENRs loading on minimum torque of the $CaCO_3$ filled NR compounds

Figure 5 shows that the additions of 5.0 phr of each type of the ENRs slightly 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 [14]. 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 was further increased. In this case, the ENRs might be considered as compatibilizers in the $CaCO_3$ filled NR compounds.

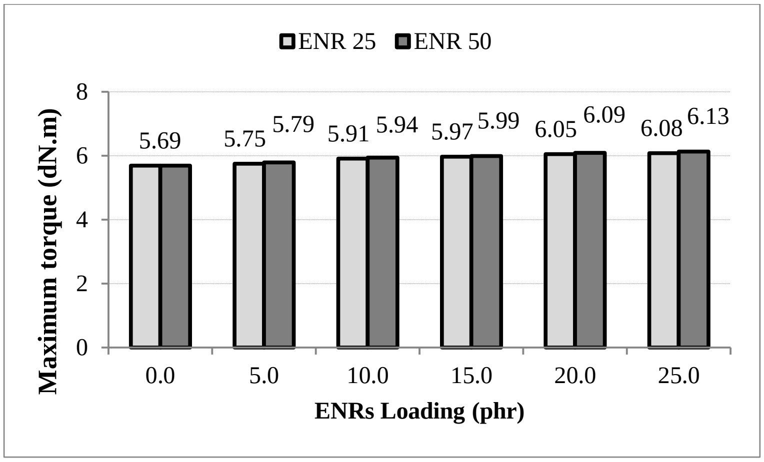

Figure 5. The effect of ENRs loading on maximum torque of the $CaCO_3$ filled NR compounds

Figure 6 shows the effect of ENRs on the torque difference (M_H—M_L) of the $CaCO_3$ filled NR compounds. It is believed that torque difference indicates the total crosslink density of a rubber compound [14-16]. The greater the torque difference, the higher is the total crosslink density. Generally, the total crosslink density of a rubber compound contains sulphide and physical crosslinks [17, 18]. ENRs can undergo 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 $CaCO_3$ filled NR compounds might contain sulphide, ether and physical crosslinks due to the presence of ENR.

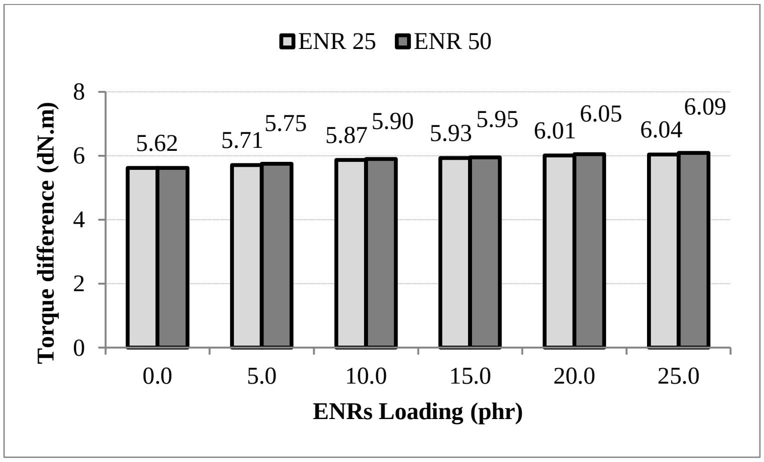

Figure 6. The effect of ENRs loading on torque difference of the $CaCO_3$ filled NR compounds

As shown in Figure 6, the addition of 5.0 phr of ENR 25 or ENR 50 increased the torque difference ($M_H—M_L$) of the control compound. 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 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 [18, 19].

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 compounds. ENR 50 systems with more epoxide groups produced a higher degree of additional ether crosslinks than ENR 25 systems.

The rubber - filler interaction

The rubber - filler interaction, based on the Lorenz and Park's equation is shown in Figure 7. For both ENRs systems, it can be seen that the Qf/Qg values were decreased by increasing the ENRs loadings from 5.0 to 25.0 phr. A lower Qf/Qg value indicates a greater rubber - filler interaction [8, 10]. A greater degree of rubber - filler interaction of the filled compounds with ENRs was attributed not only to the additional rubber phase amount (as discussed earlier) but also to the polarity of ENRs. Due to the presence of epoxide groups, ENRs are polar rubbers and they are relatively compatible with polar fillers such as $CaCO_3$ and silica compared NR. Surely, such compatibility should produce a greater rubber - filler interaction.

At a similar ENR loading, the rubber - filler interactions of ENR 50 were greater than those of ENR 25. It was simply attributed polarity degree of those ENRs. Compared to ENR 25, ENR 50 has more epoxide groups and hence, makes it more polar and it has a stronger interaction with $CaCO_3$.

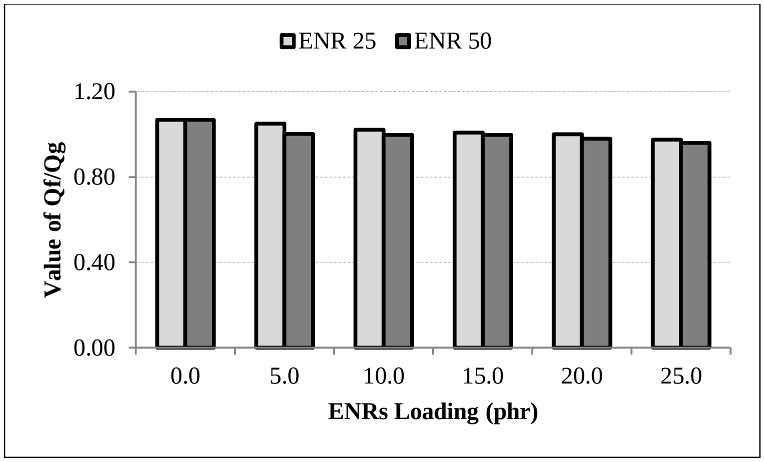

Figure 7. The effect of ENRs loading on Qf/Qg values of the $CaCO_3$ filled NR compounds

The total crosslink density

The effect of ENRs on the total crosslink density of the $CaCO_3$ filled NR vulcanisates is shown in Figure 8. The total crosslink density was determined by the Flory—Rehner approach. The additions of 5.0 phr of each ENRs into the $CaCO_3$ filled NR compound 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 Figure 6. This surely confirms that torque difference indicates the degree of crosslink density of the filled NR compounds. 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.

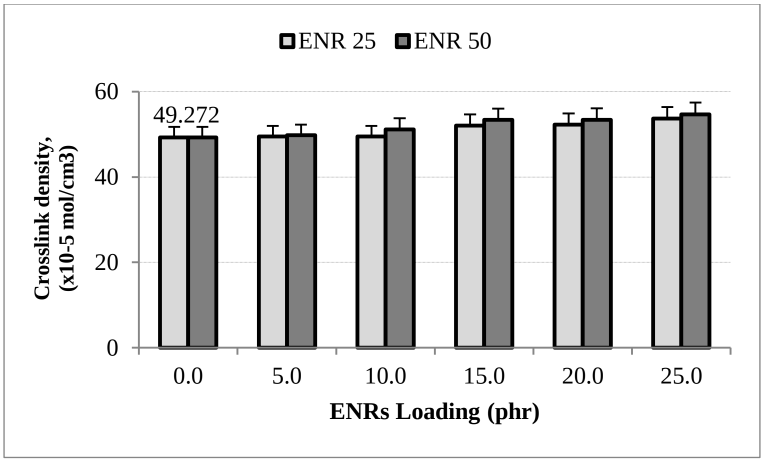

Figure 8. The effect of ENRs loading on crosslink density of the $CaCO_3$ filled NR compounds

Conclusion

Epoxidized natural rubbers functioned as curatives ingredients in calcium carbonate filled natural rubber compounds. They decreased the scorch and cure times; increased the maximum torque and torque difference of calcium carbonate filled natural rubber compounds. Epoxidized natural rubbers also functioned as compatibilizers. They improved the filler dispersion, rubber - filler interaction and crosslink density of calcium carbonate filled natural rubber compounds. The higher the loading of epoxidized natural rubber in the calcium carbonate filled natural rubber compounds; the more pronounced were the curative and compatibilization effects. At a similar loading, the curative and compatibilization effects of epoxidized natural rubber with 50 mol epoxidation were higher than those of epoxidized natural rubber with 25 mol epoxidation.

Acknowledgement

The authors would like to thank the Directorate General of Higher Education Ministry of Education and Culture of Republic Indonesia for a research grant (Penelitian Fundamental, 1608/UN5.1.R/KEU/2012) and Universiti Sains Malaysia for providing the materials and research facilities.

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