The Effect of Epoxidized Natural Rubber as A Compatibilizer on the Properties of Standard Malaysian Rubber/Ethylene Propylene Diene Monomer Blends

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Abstract. In this study, the effects of epoxidized natural rubber (ENR-50) as compatibilizer on the properties of Standard Malaysian Rubber/Ethylene Propylene Diene Monomer (SMR L/EPDM) blend were investigated. Standard Malaysian Rubber/Ethylene Propylene Diene Monomer/Epoxidized Natural Rubber (SMR L/EPDM/ ENR-50) blends were prepared by two-roll mill with five different compositions (i.e., 80/20/0, 80/20/1, 80/20/3, 80/20/5, 80/20/7 and 80/20/10), which the (SMR L/EPDM) content fixed at 80/20 which is the optimum ratio for (SMR L/EPDM) depending on our previous study. Cure characteristics, mechanical properties studies were performed to determine the compatibility of SMR L/EPDM blends in the presence of ENR-50 as a compatibilizer. The optimum cure characteristics showed by SMR L/EPDM blends with the presence of ENR-50, which lower scorch time $t_2$ and cure time $t_{90}$ and increase the cure rate index CRI. In addition, SMR L/EPDM blends with the presence of ENR-50 have improved the physical properties such as swelling test, crosslink density and hardness test.

1. Introduction
Polymer blend is conducted to achieve desired requirements that cannot be obtained by the current available individual polymer. In addition, blending of rubbers introduces a superiority to the physical properties of the final vulcanized product [1, 2]. Unfortunately, the blending of two rubbers sometimes leads to immiscibility, which depends on the individual properties of each rubber. As a result, the
desired properties will not be gained without a third component. The compatibilizer is one of the solutions of this problem, which is able to mediate an attractive interaction between the phases [3].

The interfacial adhesion can be improved either interact chemically with both phases or will have a specific interaction with one phase and a physical interaction with other. The compatibilizer may form an interface between the immiscible blend components so that imposed stresses can be transferred between the phases via covalent bonds along the copolymer backbone. However, it is important to understand the blend morphology because it has a strong effect on the properties of polymer blends [4].

Epoxidized natural rubber (ENR-50) is manufactured from natural rubber by chemical modification method, by changing some of the double bonds with epoxide parts and contains 50 mol% of the epoxide group. ENR-50 is a polar rubber and possesses properties similar to some of synthetic elastomers. It has reported that with the increasing of the ENR’s polarity, the compatibility of ENR-50 will increase. That is because of the presence of the epoxide groups in ENR, which introduces polarity and make it more attractive for rubber-rubber or rubber-plastic blending industry [5].

According to the polarity, ENR-50 is miscible with the polar rubbers such as ethylene propylene diene monomer (EPDM), thereby offering significant properties as well as high strength. In this work, the effect of ENR-50 as a compatibilizer on the cure characteristics and physical properties of standard Malaysian rubber/ethylene propylene diene monomer (SMR L/EPDM) blends were carried out.

2. Experimental

2.1. Materials

Standard Malaysian natural rubber grade L (SMR L) and ethylene propylene diene monomer (EPDM) rubber were supplied by Rubber Research Institute Malaysia (RRIM). Epoxidized natural rubber (ENR-50) that used as a compatibilizer was purchased also from Rubber Research Institute Malaysia (RRIM). The other chemicals that used in the compounding process such as zinc oxide and steric acid (S. A.) as activators, N-cyclohexyl-2-benzothiazole sulphonamide (CBS) as accelerator, butylated hydroxytoluene (BHT) as antioxidant and sulphur as vulcanizing agent were supplied by Anchor Chemical Co. (M) Ltd.

2.2. Formulation and testing of CR/ rNR-G compounds

The SMR L/EPDM/ ENR-50 blends were prepared by two roll mill. The different parts per hundred resin (phr) of ENR-50 were used i.e., 0, 1, 3, 5, 7 and 10, whereas the weight percent of SMR L and EPDM was maintained at 80 and 20, respectively, as the optimum ratio was selected from series (based on 1st series). The (80/20/1, 80/20/3, 80/20/5, 80/20/7 and 80/20/10) ratios were compared to the control ratio (80/20/0).

2.3. Characterizations and testing of CR/ rNR-G compounds

After compounding process, rubber compounds were taken out from freezer and defrozen at room temperature for 30 minutes for the purpose of curing characteristic test. curing characteristic test was done by using Rheometer Model HT-M2000. Rheometer was heated until achieve the desired curing temperature which is 160 °C. The test was run for 20 minutes. 4.0 g of uncured compound rubber was weighed and placed on the heated rotor. and the heated top die cavity was immediately brought down on to the lower dies thus filling the cavity. The machine plots a graph of torque verses time. Curing characteristic such as minimum torque $M_L$, maximum torque $M_H$, cure time ($t_{90}$) and scorch time ($t_2$) Were obtained.

2.4. Hardness Test

Hardness of the samples was measured according to ASTM D-2240-81 using a Shore A type durometer which employed a calibrated spring to provide the indenting force. Since the hardness reading decreased with time after establishment firm contact between the indentor and the sample, the recording immediately after establishment to firm contact were taken. The measured values of
hardness were obtained at three different points distributed over test piece. Three test pieces were used and their average value was determined.

2.5. Swelling Test and Crosslink Density
A cured test piece of above dimension was weighed using an electronic balance before swollen in toluene. After that, all parts of test piece were fully immersed in toluene. After 48 hours, test piece was taken out, wiped, weighed again rapidly. Swelling bottle that contains test sample and toluene need to be closed neatly because of rapid evaporation of toluene. Precautions need to be taken into account during handling toluene because this solvent is hazardous. Swelling percentage was calculated by the equation 1.

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\text{Swelling percentage} = \left( \frac{M_2 - M_1}{M_1} \right) \times 100
\]

Where \( M_1 \) is the initial mass of the tested piece (g) and \( M_2 \) is the mass of it after swollen in toluene.

3. Results and discussion

3.1. Cure Characteristics
The effect of ENR-50 as a compatibilizer on the scorch time (\( t_2 \)), cure time (\( t_{90} \)), Minimum Torque (\( M_L \)) and Maximum Torque (\( M_H \)) of SMR L/EPDM blends is shown in Table 1, figure 1 and 2.

| ENR-50 (phr) | Minimum torque \( M_L \) (dNm) | Maximum torque \( M_H \) (dNm) |
|--------------|---------------------------------|-------------------------------|
| Control      | 3.05                            | 14.40                         |
| 1            | 2.65                            | 11.95                         |
| 3            | 3.22                            | 13.70                         |
| 5            | 3.60                            | 15.85                         |
| 7            | 3.27                            | 16.90                         |
| 10           | 2.95                            | 15.65                         |

From the results that illustrated in figure 1, it can be seen that with the increasing of ENR-50 content, \( t_2 \) of the rubber compounding also increased till reached the ratio 5 phr. After that decreased gradually from 7 phr until 10 phr. Generally, the addition of ENR-50 led to increase crosslink density and shorter scorch time because the epoxy ring in ENR-50 activates the transformation of adjacent double bonds in the rubber molecules into free radicals. These radicals can quickly react and form additional crosslink with sulfur. But, the increasing of ENR-50 concentration caused a dilution of the curing agent content and an increase in the viscosity, that was resulted in a stoichiometric imbalance and led to a change in the reaction mechanisms. In addition, the increasing of ENR-50 content caused an increasing in the molecular weight of the epoxy during curing. This led to the formation of a second rubbery phase, all these reasons were a result to increase the scorch time with the increment of ENR-50 ratio [6].
Figure 1. Scorch time of SMR/(EPDM) with different ENR-50 loading.

Figure 2 illustrates the effect of ENR-50 as a compatibilizer on the cure time (t₉₀) of SMR L/EPDM blends. The results showed that the optimum t₉₀ value of the blends were found by adding of ENR 50 at 1 phr but after this ratio there is no significant change with the increasing of ENR 50 content. The shorter cure time shown by SMR L/EPDM with addition 1 phr ENR 50 due the presence of ENR 50 which catalyzed the crosslink reaction [3].

Figure 2. Cure time of SMR/(EPDM) with different ENR-50 loading.

In addition, Figure 3 shows a cure rate index (CRI) of SMR L/EPDM filled ENR 50. It has denoted that the cure rate index (CRI) decreased until 7 phr and increased gradually up to 10 phr of ENR 50 loading. The decreased in cure rate index with increasing ENR-50 content might be due to the lower viscosity. In blends, the lower viscosity component tends to form a continues phase which it will become the more ingredient govern the curing process [7]. The SMR L/EPDM with addition at 1 phr of ENR 50 shows the optimum cure rate index. It can be seen that at this loading, the rubber matrix is filled with 1 phr of ENR 50 content tend to crosslink efficiently.
Minimum torque is related to the viscosity after addition of ENR-50. It can be seen that the trend increased gradually from 1 until 5 phr loading and it started decreasing gradually to 10 phr loading. At 1 phr of ENR 50 showed the lowest minimum torque compared to the control and different loading of ENR 50, which it can be selected as the optimum minimum torque value in this series. This result was attributed to the effect of the adjacent double bond of the oxirane group of ENR 50, which provides an acceleration in the vulcanization reaction [8].

Furthermore, the result showed an increasing in the maximum torque significantly with the increasing of ENR 50 loading. Similarly, the maximum torque values decreased from 7 to 10 phr. Maximum torque values were determine a measurement of the stock modulus, which increases the interaction between the rubber matrix and the compatibilizer. Moreover, as can be seen, the lowest value of maximum torque showed by 1 phr of ENR 50 addition and it also selected as the optimum maximum torque in this series. This can be explained by the poor interaction between rubber matrix and ENR 50 [3].

3.2. Hardness Test
Table 2. shows the effect of hardness test on SMR L/EPDM blends with different loading ENR 50. As can be seen that, the hardness values increased with the increasing of different loading of ENR 50 until reached 5 phr and started to decrease gradually until 10 phr. The addition of different loading of ENR 50 showed values higher than the control value. However, SMR LIEPDM blend at 1 phr was selected as an optimum value of hardness compared to other values. This indicate that, the flexibility and elasticity of the rubber chain were less when ENR 50 at 1phr loading incorporated into rubber matrix, which also in more rigid rubber vulcanizate and increased the hardness. This observation might be attributed to the addition of ENR 50 on SMR LIEPDM. Which SMR L is non-polar rubber whereas EPDM and ENR 50 are polar rubber. It is generally observed, the mechanical response of the blend is related closely with compatibility and a synergistic effect is often obtained with miscible or partially miscible blends [9].

3.3. Swelling percentages
Swelling resistance is an indicator of the degree of crosslinking because the degree of swelling is proportioned inversely to the amount of crosslink. The effect of swelling percentage on SMR L/EPDM blends with different loading of ENR 50 is illustrated in table 2. As observed swelling percentage increased while the crosslink density decreased. SMR L/EPDM blend with 1 phr loading showed the highest value compared to other different loading. The decrement of crosslink lead to the increase in molecular weight between two adjacent crosslink. Thus, the diffusion of toluene into vulcanizate was expected to be in its maximum value, which resulted in high percentage of swelling [10, 11].
Table 2. cure characteristics of (SMR)/(EPDM) with different ENR-50 loading.

| ENR-50 content (phr) | Swelling percentages (%) | Hardness test (Shore A) |
|----------------------|---------------------------|-------------------------|
| Control              | 275                       | 42.8                    |
| 1                    | 245                       | 44.3                    |
| 3                    | 238                       | 46.0                    |
| 5                    | 242                       | 46.8                    |
| 7                    | 235                       | 45.9                    |
| 10                   | 237                       | 45.4                    |

4. Summary
The addition of different contents of ENR-50 into the optimum blend ratio from series 1 made a significant effect on the cure characteristics and physical properties. The optimum blend showed by SMR L/EPDM blends with addition 1 phr of ENR 50. The ratio of 1 phr of ENR 50 showed better improvement towards the rubber compound such as curing characteristics; lowered both of $t_{90}$ and $t_2$, higher cure rate index (CRI). Meanwhile it also showed the improvement in physical properties such as swelling percentage, crosslink density and hardness test compared to other contents of ENR 50.

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