The Effects of Epoxidised Natural Rubber (ENR-50) on Cure Characteristics and Tensile Properties of Recycled Natural Rubber Catheter Filled Ethylene Propylene Diene Monomer (EPDM) Vulcanizates

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Abstract. The effect of epoxidised natural rubber (ENR-50) on cure characteristics and tensile properties (tensile strength, modulus at 100% elongation and elongation at break) of recycled natural rubber catheter filled ethylene propylene diene monomer (EPDM) vulcanizates were studied. The scorch time, t2 of EPDM/NRr blends with and without ENR-50 increased as NRr content increased while the cure time, t90 is decreased. However, with the presence of ENR-50 in EPDM/NRr blends, the t2 was longer and t90 was shorter than the uncompatibilized EPDM/NRr blends. The minimum torque, ML, of EPDM/NRr blend with and without ENR-50 relatively increased while maximum torque, MH, decreased with increasing NRr content. With the presence of ENR-50, the compatibilized EPDM/NRr blends exhibit a lower value of ML and MH compared with uncompatibilized blends. The incorporation of ENR-50 in EPDM/NRr blends enhanced the tensile strength and tensile modulus of compatibilized EPDM/NRr blends compared to uncompatibilized EPDM/NRr blends. The elongation at break (EB) of compatibilized EPDM/NRr blends is lower than the uncompatibilized

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EPDM/NRr blends at all blend ratios. This indicated that ENR 50 improved the curing characteristics and tensile properties of the compound.

1 Introduction

In many applications, such as automobiles, boots, toys, and others, the wide use of rubber materials has resulted in high post-consumer waste production. This rubber wastes significantly contribute to environmental pollution, due to the presence of three-dimensional networks in rubber goods, such rubber waste does not degrade rapidly. Poor disposal of rubber goods globally is a possible threat to human health or even to the living and decreases environmental quality [1].

The emergence of a higher percentage of rubber discarded in rubber industries is due to the unstable nature of the rubber compound and the strict quality requirements of the rubber products. Such discarded rubbers contain about 95% very high-quality rubber hydrocarbons, which are just slightly cross-linked [2]. These rejects, if not used accordingly, may cause severe environmental and ecological problems. An example of the rejected rubber product is the catheter which is mainly used in the medical and health care facilities. A catheter is a flexible tube inserted into some part of the body which provides a fluid passage channel or a medical device.

In this study, the effect of epoxidised natural rubber (ENR-50) of recycled natural rubber catheter filled ethylene propylene diene monomer (EPDM) vulcanizates on tensile properties such as tensile strength, modulus at 100% of elongation and elongation at break will be determined. Besides, the effect on the cure characteristics also will be studied.

2 Materials and Methods

2.1 Materials

Epoxidized natural rubber (ENR-50) was used as a compatibilizer in this study. Filler used were recycled natural rubber catheter (NRr) and ethylene propylene diene monomer (EPDM). Other additives used were Ncyclohexyl-2-benzothiazole sulfonamide (CBS), zinc oxide, sulphur and stearic acid. All materials are listed as shown in Table 1 within their respective source.

| Materials                        | Description       | Source                        |
|----------------------------------|-------------------|-------------------------------|
| EPDM                             | Elastomer         | Malaysian Rubber Board       |
| ENR-50                           | Compatibilizer    |                               |
| Recycled Natural Rubber Catheter | Filler            | Teleflex Medical Sdn. Bhd.    |
| CBS                              | Accelerator       | Anchor Chemical Co (M) Ltd.   |
| Zinc oxide                       | Activator         |                               |
| Stearic acid                     | Vulcanizing agent |                               |
| Sulphur                          |                   |                               |

2.2 Compounding

The recycled natural rubber catheter (NRr) powder forming was done in a grinder machine (RT-34 Vertical High-Speed Pulverizing Machine) using 100 mesh (149 microns). ENR-50
was mixed using a two-roll mill for all the compounding ingredients. The rubber vulcanizates were prepared using different formulations, as shown in Table 2. The EPDM/NRr blends with ENR-50 were formulated with mixing ratios of 80/10/10, 70/20/10, 60/30/10, 50/40/10 and 40/50/10 respectively.

Table 2. The formulation for recycled natural rubber catheter filled EPDM vulcanizate.

| Ingredients (phr) | Blend |
|------------------|-------|
|                  | R10   | R20   | R30   | R40   | R50   |
| EPDM             | 80    | 70    | 60    | 50    | 40    |
| NRr              | 10    | 20    | 30    | 40    | 50    |
| ENR-50           | 0/10  | 0/10  | 0/10  | 0/10  | 0/10  |
| Zinc oxide       | 5     | 5     | 5     | 5     | 5     |
| Stearic acid     | 2     | 2     | 2     | 2     | 2     |
| Sulfur           | 2     | 2     | 2     | 2     | 2     |
| CBS              | 1     | 1     | 1     | 1     | 1     |

2.3 Measurements

2.3.1 Cure characteristics

The cure characteristics such as scorch time (t2), cure time (t90), minimum torque (M_L) and maximum torque (M_H) were measured using a rheometer model HT-M 2000 operated at 160°C according to ASTM D5289.

2.3.2 Mechanical properties

The dumbell-shaped samples were prepared according to ASTM D-412 for tensile testing [3]. The tensile test was performed at a crosshead speed of 500mm/min using Instron Machine. Tensile strength, elongation at break and modulus at 100% elongation (M_{100}) were measured.

3 Results and Discussion

3.1 Cure Characteristics

The results of scorch time (t2) and cure time, t90 of EPDM/NRr blends with and without ENR-50 are displayed in Fig. 1. It was observed that the t2 of EPDM/NRr blends with and without ENR-50 relatively increased as NRr content increased. This shows that the NRr has higher scorch times than the EPDM resulting in the increase in scorch time of the blends of both rubbers. The high value for R10 and the decrease for R50 with ENR-50 because the amount of mastication during mixing varies. The EPDM/NRr blends with ENR-50 exhibit longer scorch times than EPDM/NRr without ENR-50 which indicates improved processability after compatibilization of the blends [2].
Fig. 1. The scorch time, $t_s$ and cure time, $t_{90}$ of EPDM/NRr blends with and without ENR-50. It also can be seen that cure time, $t_{90}$ of EPDM/NRr blends with and without ENR-50 decreased as NRr content increased as shown in Fig. 1. As for the cure rate, NRr-rich blends displayed lower cure rates than the rich EPDM blends. The initial cure time value that is higher than NRr-rich blends can be due to the low efficiency of EPDM when vulcanized with the sulfur system, as well since EPDM has relatively low diene content [5]. It is also found that an increase in NRr content in rubber blends reduces cure time due to the presence of crosslinked precursors and unreacted curatives in recycled rubber, thus accelerating the vulcanization process [3].

Fig. 2. The minimum torque, $M_L$ and maximum torque, $M_H$ of EPDM/NRr blends with and without ENR-50. The minimum torque, $M_L$, of EPDM/NRr blends with and without ENR-50 is relatively increased with increasing NRr content as displayed in Fig. 2. This is possibly due to the presence of cross-linked NRr rubber and other additives. Once the content of NRr increases in the EPDM/NRr blends, the flowability of the blends is restricted and thus the $M_L$ is increased. However, the EPDM/NRr blends with ENR-50 showed lower $M_L$ especially in contrast to EPDM/NRr blends without ENR-50. This suggests improved processability after compatibilization of the blends [2].

Fig. 2 also shows the maximum torque, $M_H$, of EPDM/NRr blends without ENR-50 relatively decreased as NRr content increased. As the filler itself is rubber in this situation, the combined effect of cross-link density variation and the existence of cross-linked particles may result the variation. At 10 phr of NRr content, the presence of cross-linked particles...
increases $M_H$, but sulfur migration is predominant at later stages of processing, leading to reduced cross-link densities [2]. This causes a reduction in $M_H$ values. It is also can be seen that EPDM/NR blends with ENR-50 relatively showed a lower value of $M_H$ than EPDM/NR blends without ENR-50. By reducing the stiffness of the compound, this proves that the ENR-50 improves the blends.

3.2 Tensile Properties

The tensile strength of EPDM/NR blends with and without ENR-50 is shown in Fig. 3. Overall, both EPDM/NR blends showed the same trend, with reduced tensile strength as NR content equivalent to the EPDM content. These findings are due primarily to the blends being incompatible.

NR content in the blend mainly attributed to the tensile strength of these binary blends. Binary NR and EPDM blends were incompatible and demonstrated weak interfacial adhesion, leading to poor strength properties. As the filler content increases, the tensile strength increases significantly and reaches a maximum value at 30 phr content. This is primarily due to the presence of the crosslinked structure in the recycled natural rubber [5]. The tensile strength values show a decrease or leveling-off behavior beyond the 30 phr material. There will be a strong tendency for agglomeration at higher filler loading, which can diminish the interfacial bonds [2]. Therefore, tensile strength drops suddenly.

Nevertheless, the tensile strengths of the EPDM / NR blends have been enhanced with the inclusion of ENR-50 in EPDM / NR blends. This can be clarified by a better distribution of NR in the EPDM matrix with the existence of ENR-50, thus enhancing the interfacial adhesion of EPDM/NR blends by decreasing the interfacial energy between phases [2]. A contrast of the 70/30 EPDM/NR blend with and without compatibilizer presents that the tensile strength of blend with ENR-50 is higher than the blend without compatibilizer. The increase in tensile strength increases gradually up to 30 phr of NR in the EPDM/NR blend. However, with the amount of NR increased to 40 phr, the tensile strength decreases again. This is because there is no co-curing between the ENR-50 and the other rubber forms, as it has a fully saturated structure. The depletion of co-cure has a detrimental effect on the final properties [6]. It is evident that 10 phr of ENR-50 is inadequate to provide enhanced tensile properties for the blend.
Fig. 3. The tensile strength of EPDM/NRr blends with and without ENR-50.

The effect of ENR-50 on the tensile modulus ($M_{100}$) of EPDM/NRr blends is shown in Fig. 4. It does seem that for both EPDM/NRr blends with and without ENR-50, it increased gradually as NRr content is increased, the emergence of NRr into the rubber matrix has increased the vulcanizates’ stiffness. The increase in $M_{100}$ of compatibilized EPDM/NRr blends was attributed to an enhancement in cross-linking density.

With the introduction of ENR-50 as a compatibilizer in melt compounds of natural rubber composites, the tensile modulus of the natural rubber composites has been reported to increase due to an increase in crosslink density [3]. With the inclusion of ENR-50 in EPDM /NRr blends, partial compatibility may occur through hydrogen bonding due to the interaction between NRr and the ENR-50 epoxy group. The isolated double bond in ENR-50 deterred the formation of intra-molecular sulfide links, which increased the rate of crosslinking, leading to an increase in the modulus [3].
Fig. 4. The tensile modulus of EPDM/NRr blends with and without ENR-50.

Fig. 5 presents the effect of ENR-50 on elongation at break ($E_b$) of EPDM/NRr blends. The findings show that for EPDM/NRr blends with and without ENR-50 it decreased comparatively as NRr content increased. The increase in cross-linked density is stated to have led to a decrease in $E_b$ value [3]. It would seem that the EPDM / NRr blends with ENR-50 were lower $E_b$ than the EPDM / NRr blends without ENR-50. This finding is possibly due to the existence of various additives, crosslinked precursors and unreacted curative in the NRr itself, together with ENR-50, which impedes the flow and mobility of the EPDM/NRr blends.

Fig. 5. The elongation at break ($E_b$) of EPDM/NRr blends with and without ENR-50.
4 Conclusions

The following conclusions can be drawn from this study:

1. The scorch time, $t_2$ of EPDM/NR$_r$ blends with and without ENR-50 increased as NR$_r$ content increased while the cure time, $t_{90}$ is decreased. However, with the presence of ENR-50 in EPDM/NR$_r$ blends, the $t_2$ was longer and $t_{90}$ was shorter than the EPDM/NR$_r$ blends without ENR-50.

2. The minimum torque, $M_L$, of EPDM/NR$_r$ blend with and without ENR-50 increased while the maximum torque, $M_H$, decreased with increasing NR$_r$ content. With the presence of ENR-50, the EPDM/NR$_r$ blends exhibited a lower value of $M_L$ and $M_H$ than EPDM/NR$_r$ blends without ENR-50.

3. The incorporation of ENR-50 in EPDM/NR$_r$ blends enhanced the tensile strength and tensile modulus of compatibilized EPDM/NR$_r$ blends compared to uncompatibilized EPDM/NR$_r$ blends. The elongation at break $(E_b)$ of compatibilized EPDM/NR$_r$ blends is lower than the uncompatibilized EPDM/NR$_r$ blends at all blend ratios.

4. ENR-50 shows the effect of compatibilizer in EPDM/NR$_r$ blends by improving the curing properties and tensile properties of the compound.

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