Development of green materials from ENR-25/PHBV blends: Curing characteristics and mechanical performance

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Abstract. The objective of this work was to develop green materials from epoxidized natural rubber (25% epoxidation), (ENR-25), poly(3-hydroxybutyrate-co-3-hydroxyvalerate), (PHBV), and polybutadiene adducted with maleic anhydride, (PB-g-MA) as compatibilizer. The ENR-25/PHBV blends were prepared at the ratio of 100/0, 90/10, and 80/20 with 0 and 10 %wt. PB-g-MA. The blends were prepared using an internal mixer, where PHBV was first melted at a temperature of 175 °C before mixing with ENR-25 and the incorporation of a compatibilizer. The mixing of ENR-25 and PHBV was continued at a temperature of 175 °C and mixing speed of 50 rpm until it reaches the complete blending time. All ENR-25/PHBV blends were then mixed with curing agents in an internal mixer at a temperature of 50 °C. The cure characteristics were determined using a moving die rheometer (MDR). Then vulcanization proceeded in a compression molding machine. The result shows that the addition of PHBV enhanced the modulus of ENR-25 for every blend ratio with and without compatibilizer owing to the mechanical properties of PHBV. Significantly, the PB-g-MA compatibilizer successfully improved the interface adhesion between ENR-25 and PHBV and the decrease in phase size was clearly seen in the SEM images.

1. Introduction
Environmentally friendly materials based on renewable resources, especially biodegradable polymers, have attracted much attention due to recent environmental concerns. In this regard, natural rubber (NR) is one of the attractive biopolymers due to its several advantages, such as high flexibility, elasticity, and resilient properties. However, NR is nonpolar and poorly resistant to hydrocarbons such as oil. Thus, modification of NR has been sometimes used to improve its properties. Epoxidized natural rubber (ENR) is a modified natural rubber, produced through epoxidation at the double bonds of the monomers, resulting in epoxide groups replacement in the main chain [1]. The degree of epoxide groups (such as 25 and 50% epoxidation) can be controlled by epoxidation time or the reactant concentration [2]. Notably, ENR possesses high flexibility, good abrasion, and oil resistance. In fact, the ENR compound incorporated with organic fillers are presently being proposed for improved mechanical performance and dimension stability in different applications. However, it should be noted that ENR is capable of...
crosslinking within and between their molecules and this may cause a lower level of microbial attack in the biodegradable process. Typically, biodegradable materials were used to prepare green biodegradable thermoplastic natural rubber based on ENR/PBS, ENR/PHBV and ENR/PLA blend to enhance the biodegradability [3-5]. On the other hand, rigid polymers are potentially used as inorganic fillers since their phase morphology can be controlled by processing conditions. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), (PHBV), is a type of poly(3-hydroxyalkanoate). It is an aliphatic polyester produced by the fermentation process of bacterial such as Alcaligenes eutrophus, Bacillus, and Pseudomonas under controlled oxygen and carbon dioxide environment [6]. Interestingly, PHBV is a biodegradable thermoplastic with several fascinating features such as high mechanical properties, non-toxic properties, and complete biodegradability under composting, backyard, and landfill conditions [7-8]. Therefore, the incorporation of PHBV into ENR is quite interesting since both are natural-based materials. Several studies have reported that when the carboxyl end group of PHBV is reacted with the epoxide group of ENR-25 bonding occurs the ENR-25 and PHBV chains. This will invariably result in notable improvement in phase compatibility between these materials [4,9-10]. Nevertheless, compatibilizers may be added into the blends to enhance interfacial adhesion and improve the mechanical properties [11-12].

Therefore, this work aimed to develop alternative green materials by incorporating PHBV into ENR-25. The compatibility between PHBV and ENR-25 in the blends was improved by using PB-g-MA. Then the curing characteristics, mechanical properties, and fractural morphology of ENR-25/PHBV blends were investigated.

2. Experimental

2.1. Materials
The epoxidized natural rubber with a 25% epoxidation level (ENR-25) was purchased from Muang Mai Guthrie Pub Co., Ltd., Thailand. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV, ENMAT Y1000P) was purchased from Ningbo Tianan Biologic Material Co., Ltd., China. Polybutadiene added with maleic anhydride (PB-g-MA, Ricobond® 1756) used as a compatibilizer was manufactured by Cray Valley USA, LLC. The other chemical, such as the sulfur used as vulcanizing agent, Tetramethylthiuram disulfide (TMTD) and N-cyclohexyl-2- benzothiazole sulfonamide (CBS) used as accelerators, Zinc oxide and Stearic acid used as activators, and Ozone wax were purchased from the Rubber Authority of Thailand. The PHBV pellets were dried in an oven for 12 h at 50 °C before use.

2.2. Preparation of ENR-25/PHBV blends and vulcanization
The ENR-25/PHBV blends were prepared via the melt blending method using an internal mixer. The dried PHBV was first added in an internal mixer at 175 °C with a rotating speed of 50 rpm for 5 min to soften the PHBV. Then, ENR-25 and PB-g-MA were added, and the mixing was continued for another 10 min. The weight ratios of the ENR-25 to PHBV were prepared as follows: 100/0, 90/10, and 80/20. To investigate the effect of compatibilizer, the blends without and with 10%wt. PB-g-MA were also prepared. The ENR-25/PHBV blends with and without compatibilizer were mixed with the vulcanizing ingredients, comprising of 2.6 phr of ZnO, 1.5 phr of Stearic acid, 1.9 phr of CBS, 0.9 phr of TMTD, and 1.6 phr of Sulfur for the compounding process. The curing temperature and time were obtained from MDR characterization. The sample sheets were then prepared by compression, prior to testing.

3. Characterization

3.1. Moving die rheometer (MDR)
The cure characteristics of the neat ENR-25 and the ENR-25/PHBV blends were studied using a rheoTECH MD+ (Montech, China). A sample of approximately 3.00 g of blends was placed in the
rotating discs. Then the cure characteristics were investigated at four different curing temperatures such as 140 °C, 150 °C, 160 °C, and 170 °C.

3.2. Universal testing machine (UTM)

The tensile properties of the neat ENR-25 and its blends were examined according to ASTM D 412 using a Universal Testing Machine (Tinius Olsen) with Horizon software package (Calserve, Thailand) with a 5 kN load cell at a crosshead speed of 500 mm/min. The tensile strength, modulus at 300% strain (M300), and elongation at break were reported as the average of five tested dumb-bell specimens.

3.3. Scanning electron microscope (SEM)

The morphology of the fractured surfaces of the blends were investigated using scanning electron microscope JSM-6480LV (Jeol, Japan). A gold coated layer was subsequently applied by using an SPI module sputter coater (Structure Probe, Inc., USA). The SEM images were obtained with a voltage of 15 kV at magnifications of 300x, and 1000x.

3.4. Thermogravimetric analysis (TGA)

The thermal stability of the neat ENR-25 and its blends were examined using STA2500 (Netzsch, Germany) TGA analyzer at a temperature range between room temperature and 600 °C, under N₂ atmosphere.

4. Results and discussion

4.1. Cure characteristics

The cure characteristics of the scorch time (tₛ), cure time (t₅₀), minimum torque (Mₛ), maximum torque (M₉₀), and torque difference (M₉₀-Mₛ) are presented in Table 1 at different observed temperature. It is evident from the figure that for the neat ENR-25, the scorch and curing time decreased with increasing temperature. This is because temperature acts as an accelerator to promote the reaction [13]. The M₉₀ and M₉₀-Mₛ in the table represents the elastic modulus and crosslinking density. It was observed that the M₉₀ and M₉₀-Mₛ values increased when the temperature increased from 140 °C to 150 °C. However, at high temperatures (160 °C and 170 °C), the values decreased. This indicates that the crosslinking density decreases when the curing temperature increased. At high temperatures, the crosslinked structure was subjected to decay thereby resulting in the reduction of M₉₀ and M₉₀-Mₛ. [14-15].

| Temperature | tₛ(min) | t₅₀(min) | Mₛ(lbf*In) | M₉₀(lbf*In) | M₉₀-Mₛ(lbf*In) |
|-------------|---------|----------|------------|-------------|-----------------|
| 140°C       | 2.01    | 2.95     | 0.16       | 6.45        | 6.29            |
| 150°C       | 1.28    | 1.76     | 0.15       | 6.50        | 6.35            |
| 160°C       | 0.94    | 1.22     | 0.27       | 5.77        | 5.50            |
| 170°C       | 0.59    | 0.87     | 0.19       | 5.46        | 5.27            |

Table 2 summarizes the cure characteristics of the ENR-25/PHBV and ENR-25/PHBV/PB-g-MA blends. To compare the melting of PHBV and crosslink formation in the rubber phase, the curing was investigated at 160 °C. Significantly, the neat ENR-25 showed a shorter scorch time compared to the other blend samples. On the other hand, the ENR-25/PHBV blends without compatibilizer gave shorter tₛ and t₅₀ than the blends containing PB-g-MA. The addition of other components containing functional groups possibly absorbs the free radicals formed during vulcanization on their surface thereby resulting in the decrease of curing rate. Therefore, it can be inferred that the combination of PHBV and PB-g-MA in ENR resulted in the retardance of crosslinking reaction from their carbonyl and epoxide groups [16].
Table 2. Cure characteristics of the blends at temperature of 160 °C

| Blends                     | $t_{92}$ (min) | $t_{99}$ (min) | ML (Ibf\textperiodcentered ln) | MH (Ibf\textperiodcentered ln) | $M_H-M_L$ (Ibf\textperiodcentered ln) |
|----------------------------|----------------|---------------|-------------------------------|-------------------------------|----------------------------------------|
| 100ENR-25                  | 0.94           | 1.22          | 0.27                          | 5.77                          | 5.50                                   |
| 90ENR-25/10PHBV            | 1.58           | 2.84          | 0.15                          | 5.96                          | 5.81                                   |
| 90ENR-25/10PHBV/PB-g-MA    | 3.73           | 4.48          | 0.45                          | 4.05                          | 3.60                                   |
| 80ENR-25/20PHBV            | 2.17           | 2.46          | 0.15                          | 3.37                          | 3.22                                   |
| 80ENR-25/20PHBV/PB-g-MA    | 3.92           | 4.72          | 0.54                          | 5.03                          | 4.49                                   |

4.2. Mechanical properties

Figure 1 shows the tensile strength (TS), elongation at break (EB), and modulus at 300% strain (M300) of the neat ENR-25 and ENR-25/PHBV blends. The addition of PHBV into ENR-25 led to the decline of tensile strength and elongation at break. In contrast, all the blends showed a higher value of M300 than that of the neat ENR-25, which is an indication of improved stiffness. The stiffness of materials is the ability of such material to prevent the deformation of their shape under stress. Therefore, M300 is one of the important properties that needs to be considered for elastic materials. In the blends, the increase in PHBV content from 10 wt% to 20 wt% decreased the TS and EB due to the poor adhesion between the phases. Significantly, the blends containing the compatibilizer (C, E) shows higher TS and EB values than those without compatibilizer. This suggests that the compatibilizer improves the interfacial adhesion through interactions between the functional groups. This is because PB-g-MA contains anhydride and carboxylic groups that could strongly interact with the epoxide groups of ENR-25 and the carboxyl group of PHBV phases. However, the addition of compatibilizer resulted in the reduction of M300. This could possibly indicate that the phase size of PHBV was reduced, and it became more compatible with ENR-25.

By comparing the strength, elasticity, and stiffness of the samples it can be concluded that the 90ENR-25/10PHBV containing compatibilizer has the greater potential to achieve the desired properties of green materials.
4.3. Morphology
The scanning electron micrographs from the tensile fractured surfaces of the neat ENR and all the prepared blends are shown in Figure 2. As presented in the figure, the neat ENR-25 exhibited a smooth surface with small agglomeration of additives. However, the phase separation morphology was shown for ENR-25/PHBV blends at all blending ratios. The 90ENR-25/10PHBV blend showed large holes, which is believed to be the pull-out holes following the pull-out of PHBV droplets from the ENR matrix. In contrast, the 80ENR-25/20PHBV showed interconnected droplet shape (string shape) with some large PHBV droplets as its content increased. On the other hand, the blends containing PB-g-MA (used as compatibilizer) reveals two phases, but the size of the PHBV phase was decreased and gave better dispersion than the blends without compatibilizer. The transformation of phase shape could be obviously seen in 80ENR-25/20PHBV, as the shape changes from a linear shear interconnected shape to a droplet form after the incorporation of compatibilizer. It is noteworthy that the morphology images support the mechanical properties discussed in the previous section. Therefore, it can be inferred that the compatibility of PHBV and ENR-25 was successfully improved using the PB-g-MA as a compatibilizer.

Fig. 2. SEM of fractured surface of the blends

4.4. Thermogravimetric analysis (TGA)
The TGA curves of the neat ENR-25 and all the prepared blends are illustrated in Figure 3. As presented in the figure, the neat ENR-25 exhibited a one-step degradation pattern at a higher temperature than those of the blends. This is because the neat ENR-25 has higher crosslink density, which can be confirmed from the $M_h$-$M_L$. The degradation temperature of ENR-25 was found to be around 374.9 °C. In contrast, the ENR-25/PHBV blends showed two-step degradation patterns at the temperature around 250 °C and 370 °C, which corresponds to the degradation temperatures of PHBV and ENR-25, respectively. The addition of a compatibilizer was found to increase the degradation temperature of the blends, which indicates notable improvement in the compatibility of ENR-25 and PHBV, and the increase in crosslink density.

Fig 3. TGA of the ENR-25/PHBV and ENR-25/PHBV/PB-g-MA blends
5. Conclusion
In this study, the ENR-25/PHBV blends were prepared as an alternative green material. The cure characteristics revealed that increasing temperature accelerates the crosslinking reaction rate. However, extremely high temperature results in scission of the rubber network. The addition of other components, such as PHBV and PB-g-MA retarded the crosslinking reaction. The modulus at 300% strain (M300) indicated that the incorporation of PHBV successfully improves the stiffness of ENR-25. Furthermore, it was observed that PB-g-MA can be used as a compatibilizer to improve the compatibility between ENR-25 and PHBV as confirmed through the morphology, mechanical properties, and thermal stability measurements. In summary, the blend containing 10 wt% PHBV and compatibilizer, PB-g-MA, has a potential to meet the requirement for greener rubber.

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