Cure characteristics, thermal and mechanical properties of natural rubber/synthetic rubber blends with and without compatibilizer

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Abstract

In this study, the effects of compatibilizer loading on the cure characteristics, thermal and mechanical properties of natural rubber (NR)/synthetic rubber (SR) blends have been investigated. NR was molten and mixed with six synthetic rubbers (butadiene rubber, chloroprene rubber, ethylene-propylene diene rubber, isoprene rubber, nitrile rubber and styrene butadiene rubber) with varied NR/SR weight ratios (100/0, 75/25, 50/50, 25/75 and 0/100) and compatibilizer loadings (0-5 parts per hundred of rubber, phr) on a two roll mill at 70 °C. The results obtained from differential scanning calorimetry revealed that most of the NR/SR blends both with and without compatibilizer exhibited two glass transition temperatures, indicating that the inclusion of compatibilizers (ENR-25, ENR-50 and Ultrablend-6000) did not improve the compatibility between NR and SRs. However, they could reduce the cure time by 20-50%, as compared to the neat rubber blends, suggesting the reduction in the production energy. Tensile strength of some 50/50 rubber blends with a specific amount and type of compatibilizer improved significantly. Natural rubber/butadiene rubber with 5 phr of ENR-25, natural rubber/chloroprene rubber with 5 phr of ENR-50 and natural rubber/isoprene rubber with 5 phr of Ultrablend-6000 were great examples in terms of improving the mechanical properties.

Keywords: rubber blend, natural rubber, synthetic rubber, compatibilizer, epoxidized natural rubber, Ultrablend-6000

1. Introduction

Natural rubber (NR) is well known to offer excellent mechanical properties such as high tensile strength as well as elasticity and dynamic properties. However, NR is sensitive to degradation by heat and ozone attack since it has numerous reactive double bonds on the backbone. Furthermore, oil resistance of NR is relatively poor compared to other synthetic rubbers (Kohjiya & Ikeda, 2014). To get better properties, rubber blending is an interesting alternative.

Polymer blends are being interested in a large number of applications. An interesting example can be found in tire production. NR may be blended with synthetic rubber (SR) to improve properties since a blend can offer combined features of its individual blend partner. In an effort to overcome further applications, the rubber blends can be made between two already available materials instead of making a brand new polymer.
Blending of different rubbers is the most promising strategy and has become technically important approach (Paul & Bucknall, 2000). Many blends based on NR and other SRs, such as butadiene rubber (BR) (Groves, 1998), chloroprene rubber (CR) (Ismail & Leong, 2001), ethylene-propylene diene rubber (EPDM) (Arayapranee & Rempel, 2007; Gunasekaran, Natarajan & Kala, 2007), nitrile rubber (NBR) (Kantala, Wimolmala, Sirisinha, & Sombatsompop, 2009; Sirisinha, Limcharoen, & Thunyarittikorn, 2003) and styrene butadiene rubber (SBR) (George, Ninan, Groeninckx, & Thomas, 2000) have been reported. The property of a blend depends upon blend components, blend ratio, and processing condition of blending and curing (Paul & Bucknall, 2000). Moreover, the difference in polarity between NR and SR could also bring about high interfacial tension which affects the mechanical properties of the blend. Thus, suitable type and dosage of compatibilizer are recommended.

Epoxidized natural rubber (ENR) is a chemically modified form of the cis-1,4-polyisoprene rubber, whereby some of the double bonds in NR are converted randomly into epoxide groups. It was found to work well as a compatibilizer for rubber blends. The incorporation of ENR-50 into the rubber blends enhanced cure characteristics, mechanical properties and compatibility (Nariman, Ismail, & Rashid, 2010). Besides ENR, Ultrablend-6000, which is an aliphatic hydrocarbon resin, is a commercially available compatibilizing agent for polymers. It improved the homogeneity of the rubber blends, which have different polarities. Kaesaman and Saetung (2006) used Ultrablend-6000 as a compatibilizer in the amount of 5 phr in NR/SR system and found that the compatibility of the blend was improved.

The investigation in the compatibility of different polymer blends is important. Some advanced techniques such as dielectric measurement (Saad & El-Sabbagh, 2001), dynamic mechanical analysis (Pticek, Hrnjak-Murgic, Jelencic, & Mlinac-Misak, 2007), scanning electron microscopy (Pandey, Setua, & Mathur, 2003) are extensively used for the polymer blends. The use of differential scanning calorimetry (DSC), especially in rubber blends, is rare. Thus, the aim of this present work was to employ DSC to investigate the compatibility between NR and various SR. The NR and SR were blended via a two-roll mill at 70°C under various NR/SR blend ratios (100/0, 75/25, 50/50, 25/75 and 0/100), with and without a compatibilizer (ENR-25, ENR-50 and Ultrablend-6000). The effects of compatibilizer loading on cure characteristics, thermal, and mechanical properties were reported.

2. Materials and methods
2.1 Materials

All rubbers and compatibilizers used in this research are listed in Table 1. Six different SRs were used to blend with NR, with and without incorporation of a compatibilizer. ENRs and Ultrablend-6000 were used to compatibilize the blends. These compatibilizers were characterized by Fourier transform infrared (FTIR) spectroscopy. The FTIR spectrum of ENR-50 (Figure 1a) shows strong asymmetrical and symmetrical stretching of methylene group vibrations observed near 2925 and 2859 cm⁻¹, respectively. The stretching of methyl group vibration was found at around 2963 cm⁻¹. The band at 1663 cm⁻¹ attributed to a double bond of C=C in a natural rubber. Importantly, it represented epoxy ring stretching at 1252 and 875 cm⁻¹ (Ratnam, Nasir, Baharin, & Zaman, 2000). The FTIR spectrum of Ultrablend-6000 (Figure 1b) shows the peaks near that of ENR-50 indicating that they have similar structures. The peak at 970 cm⁻¹ attributed to the C-H wagging vibrations of trans-position in alkene structure (Griffiths & Haseth, 2007). Unfortunately, the exact structure of Ultrablend-6000 is not proposed yet in academic field.
Table 1 Rubbers and compatibilizers used in the present study

<table>
<thead>
<tr>
<th>Rubbers and compatibilizers</th>
<th>Symbol</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>NR</td>
<td>STR 5L</td>
</tr>
<tr>
<td>Synthetic rubbers:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butadiene rubber</td>
<td>BR</td>
<td>BR 01</td>
</tr>
<tr>
<td>Chloroprene rubber</td>
<td>CR</td>
<td>CR 2322</td>
</tr>
<tr>
<td>Ethylene-propylene diene rubber</td>
<td>EPDM</td>
<td>EPDM 01</td>
</tr>
<tr>
<td>Isoprene rubber</td>
<td>IR</td>
<td>IR 2200</td>
</tr>
<tr>
<td>Nitrile rubber</td>
<td>NBR</td>
<td>Nancar 3345</td>
</tr>
<tr>
<td>Styrene butadiene rubber</td>
<td>SBR</td>
<td>SBR 1502</td>
</tr>
<tr>
<td>Compatibilizers:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25 mol% Epoxidized natural rubber</td>
<td>ENR-25</td>
<td>美白系列1</td>
</tr>
<tr>
<td>50 mol% Epoxidized natural rubber</td>
<td>ENR-50</td>
<td>美白系列1</td>
</tr>
<tr>
<td>Ultrablend-6000</td>
<td></td>
<td>Ultrablend-6000^\text{a}</td>
</tr>
</tbody>
</table>

^\text{a} Obtained from Rubber Research Institute of Thailand.

^\text{b} Ultrablend-6000, a commercially available additive that improves the homogeneity of polymer blends of different polarities or different viscosities.

^\text{c} Obtained from Behn Meyer Chemical (Thailand) Co., Ltd.

Figure 1 FTIR spectra of (a) ENR-50 and (b) Ultrablend-6000
Each pair of NR and SR was compounded by a two-roll mill. Details of the mixing ingredients are shown in Table 2. All mixing ingredients were used as received.

### Table 2 Ingredients of blend compounds used in this study

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>Variable (100-0)</td>
</tr>
<tr>
<td>SR</td>
<td>Variable (0-100)</td>
</tr>
<tr>
<td>Zinc oxide (ZnO)</td>
<td>5.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2.0</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.75</td>
</tr>
<tr>
<td>mercaptobenzothiazole (MBT)</td>
<td>0.5</td>
</tr>
<tr>
<td>tetramethylthiuram disulfide (TMTD)</td>
<td>1.5</td>
</tr>
</tbody>
</table>

*phr, parts per hundred of rubber

2.2 Preparation of compounded rubber blends

Rubber blends were compounded via a two-roll mill under 70°C. The formulation is shown in Table 3. In the preparation of N<sub>50</sub>(IR), for example, 200 g of NR was initially masticated for 8 min before 200 g of IR was added. After mixing for 3 min, 20 g of ZnO and 8 g of stearic acid were added. After the gap between the two rolls of machine was set at 1 mm width, the rubber blend was continued to masticate until all ingredients were thoroughly blended. MBT and TMTD were added in the amount of 2 and 6 g, respectively. After mixing for 1 min, 7 g of sulfur was added and mixed further for 3 min. The calendered mixture was taken out for thermal property measurement.

For the blend system with a compatibilizer, the rubbers were blended under the same condition as the system without a compatibilizer. The compatibilizers used in this research were 25 mol% epoxidized natural rubber (ENR-25), 50 mol% epoxidized natural rubber (ENR-50) and Ultrablend-6000. Each compatibilizer was added only into 50/50 NR/SR blends with a different amount, as shown in Table 3. In the preparation of 5N<sub>50</sub>(IR) Ultrablend-6000, for example, all ingredients were added as that of N<sub>50</sub>(IR). However, 20 g (5 phr) of Ultrablend-6000 as a compatibilizer was added and mixed after IR was added.

### Table 3 Formulation of blend compounds

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>N&lt;sub&gt;100&lt;/sub&gt;</th>
<th>N&lt;sub&gt;75&lt;/sub&gt;</th>
<th>N&lt;sub&gt;50&lt;/sub&gt;</th>
<th>N&lt;sub&gt;25&lt;/sub&gt;</th>
<th>N&lt;sub&gt;0&lt;/sub&gt;</th>
<th>xN&lt;sub&gt;50&lt;/sub&gt;</th>
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</thead>
<tbody>
<tr>
<td>NR</td>
<td>100</td>
<td>75</td>
<td>50</td>
<td>25</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>SR</td>
<td>0</td>
<td>25</td>
<td>50</td>
<td>75</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>ZnO</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.75</td>
<td>1.75</td>
<td>1.75</td>
<td>1.75</td>
<td>1.75</td>
<td>1.75</td>
</tr>
<tr>
<td>MBT</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>TMTD</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Compatibilizer</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Variable (1, 2, 5, 5)</td>
</tr>
</tbody>
</table>

*<sup>x</sup> amount (1, 2.5 or 5) of a compatibilizer in phr added only to 50/50 NR/SR blends

<sup>1</sup> SR: BR, CR, EPDM, IR, NBR or SBR

<sup>2</sup> Compatibilizer: ENR-25, ENR-50 or Ultrablend-6000
2.3 Thermal property
Measurements were made on a Perkin-Elmer compensated differential scanning calorimeter (DSC) with a nitrogen flow of 20.0±0.1 mL min⁻¹. The heating and cooling rates were set at 10°C/min.

2.4 Cure characteristics
Cure characteristics were studied using a rheometer (TECH-PRO) according to ASTM D5289-07a for 30 min at 150°C.

2.5 Vulcanization process
All blend compounds were sulfur cured and compression molded at 150°C with a force of 150 kg/cm² using a hydraulic hot press according to their respective cure time, tc90.

2.6 Mechanical properties
Tensile properties were determined on an Instron Testing Instrument using C-type Dumbbell-specimens.

3. Results and discussion

3.1 Thermal property of NR/SR blends
A DSC technique was used to determine glass transition temperatures (Tg) of all NR/SR blends. Cooling and heating rates were applied at 10°C/min from room temperature to -95°C. The Tg of the 2nd heating in DSC thermogram, which was endothermic peaks, was reported. Only one type of rubber in the rubber compound, such as NR compound, showed only one peak of Tg in DSC thermogram. There are two distinct Tg's for all blends except the NR/IR blend. Figure 2 shows a comparison of selected areas among N100, N50(BR) and N50(IR). The system containing one rubber component as N100 showed one Tg at around -65°C. Two rubber components as N50(BR) showed two Tg's at -68°C and -6°C, referring to a phase separation between the two kinds of rubber. However, two rubber components as N50(IR) showed only one peak of Tg at -65°C, which means that this pair of rubbers are compatible. This is because the chemical structures of NR and IR are identical. Other NR/SR blends with various blend ratios demonstrated two peaks of Tg in the absence of a compatibilizer.

Many types of compatibilizers were used to increase compatibilization in the incompatible blend systems (Noriman et al., 2010; Kaesaman & Saetung, 2006). Only 50/50 blend ratio of each pair of blend was studied in this work. It was found that these compatibilizers could not combine the two separated Tg peaks of each rubber component into one peak (Khantiyoo, Na-Wichien, & Moolsin, 2014; Somphaeng, Na-Wichien, & Moolsin, 2014; Aueareekul, Khotma, & Moolsin, 2013). Therefore, they were not considered to be suitable compatibilizers in terms of thermal behaviors.

3.2 Cure characteristics of rubber compounds
The effect of the amounts of a compatibilizer used in a 50/50 blend ratio on rubber cure times was determined by a rheometer. The cure time at 90% cure, tc90, was considered to be an optimum cure time. The time below tc90 gave an
uncured compound. On the other hand, the time beyond $t_{90}$ could degrade the rubber compound. Figures 3-8 show optimum cure time of each pair of 50/50 NR/SR blend with the compatibilizer loading. It can be observed that the optimum cure time of the compound containing a compatibilizer was decreased compared to the unfilled compound. At higher compatibilizer loading (5 phr), the chances of combining the two phases of rubbers with different polarity were more favorable compared to low loading and hence good rubber-rubber interaction was achieved. In the case of BR, CR, EPDM and IR blending with NR in the presence of a compatibilizer, the cure time could be reduced up to 20-50% compared to the zero compatibilizer loading.

That means the NR/SR blend compounds with a suitable amount and type of compatibilizer consume less electric energy when the rubber vulcanization is taking place.

It should be noted in Figures 7-8 that the maximum loading of Ultrablend-6000 was 5 phr, as recommended by Behn Meyer Chemical (Thailand) Co., Ltd. This compatibilizer seemed to not act suitably in the NR/NBR and NR/SBR blend systems. However, it appears from the results that the use of ENR-50 in these systems could also reduce the optimum cure time of the blend as those of NR/BR and NR/CR blends.

Figure 3 Optimum cure time of 50/50 NR/BR blend VS compatibilizer loading

Figure 4 Optimum cure time of 50/50 NR/CR blend VS compatibilizer loading
Figure 5  Optimum cure time of 50/50 NR/EPDM blend VS compatibilizer loading

Figure 6  Optimum cure time of 50/50 NR/IR blend VS compatibilizer loading

Figure 7  Optimum cure time of 50/50 NR/NBR blend VS compatibilizer loading
3.3 Mechanical properties of compounded rubber blends

Tensile strength is one of the most important properties of the rubber products because it indicates the maximum stress of the products. The effects of compatibilizer loading on tensile strength are given in Figures 9-14. A comparison between the 50/50 NR/SR blend with and without a compatibilizer showed that the tensile strength of the blends fluctuated, depending upon type of compatibilizer and pair of blends. Most of the blends exhibited an improved strength with a compatibilizer. ENR-25 as a compatibilizer, for example, showed a great improvement on tensile strength in a blend of NR/BR under the compatibilizer usage of 5 phr (Figure 9) while ENR-50 in the amount of 5 phr was suitable with NR/CR blend (Figure 10). Both ENR-25 and ENR-50 were believed to improve the compatibilization due to the crosslinking of the opened epoxy rings (Hamzah, Bakar, Khairuddin, Mohammed, & Adnan, 2012). The elongation (%) at break tended to increase with compatibilizer loading, but some started to decrease at higher loading. The elongations of the polymer blends containing ENR-25 or ENR-50 were found to follow a similar pattern as that shown in the case of tensile strength. In the NR/IR blend, DSC thermogram indicated a good compatibilization as well as improved tensile strength in the presence of Ultrablend-6000 especially in the amount of 5 phr (Figure 12). However, decreasing trends in tensile strength were also observed with the increase of ENR-50 and Ultrablend-6000 on NR/NBR blend system (Figure 13). This may be because of the difference in polarity between NR and NBR.
Figure 10 The effect of compatibilizer loading on tensile strength of the 50/50 NR/CR blend compound (primary y-axis (left) plotted as bars and secondary y-axis (right) plotted as lines)

Figure 11 The effect of compatibilizer loading on tensile strength of the 50/50 NR/EPDM blend compound (primary y-axis (left) plotted as bars and secondary y-axis (right) plotted as lines)

Figure 12 The effect of compatibilizer loading on tensile strength of the 50/50 NR/IR blend compound (primary y-axis (left) plotted as bars and secondary y-axis (right) plotted as lines)
4. Conclusion

Rubber blends between natural (NR) and synthetic rubber (SR: BR, CR, EPDM, IR, NBR or SBR) were compounded with and without a compatibilizer. The compatibilizer such as ENR-25, ENR-50 or Ultrablend-6000 was incorporated into the blends and the effect of compatibilizer loading was investigated.

NR exhibited only one glass transition temperature (T_g) at -63°C. Under the blend system with other SR, most of the NR/SR blends presented two T_g’s in DSC thermogram indicating to an incompatible blend between these rubber blends. There was only the NR/IR blend showing one T_g as that of pure NR system. Under the use of compatibilizer, the DSC thermograms of most NR/SR blends still presented two peaks of T_g. It can be concluded from this observation that these compatibilizers (ENR-25, ENR-50 and Ultrablend-6000) were not suitable in terms of thermal behaviors to combine the different phases between NR and SR.

Reduction in cure times could be observed in the blends containing the compatibilizer. The optimum cure times of some blend systems such as NR/BR, NR/CR, NR/EPDM and NR/IR were diminished up to 20-50% compared to the system without a compatibilizer.

With the addition of a compatibilizer, the tensile strengths of 50/50 NR/SR blends fluctuated depending on the pair of rubber blends and the type of compatibilizer. In the presence of a compatibilizer, most of the rubber blends showed improved tensile properties. Examples of a suitable
dosage and type of compatibilizer on NR/SR blends were 5 phr of ENR-25 in NR/BR blend, 5 phr of ENR-50 in NR/CR blend, and 5 phr of Ultrablend-6000 in NR/IR blend. The elongations at break of all polymer blends except NR/NBR were improved with the addition of a compatibilizer and followed a similar pattern to those of the tensile properties.

5. Acknowledgements

The author gratefully acknowledges the Rubber Research Institute of Thailand for assistance throughout the work. I wish to thank Behn Meyer Chemical (Thailand) Co., Ltd. for supplying Ultrablend-6000. I am also indebted to Dr. Nikki K. Robishaw (Department of Chemistry, Faculty of Science, University of Akron, USA) for English language editing.

6. References


