EFFECT of blend ratio and compatibilizer on solution casted treated waste natural rubber latex/polystyrene blends

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Abstract

Natural rubber latex waste (WL) was treated with natural rubber latex (NRL) prior to blend with polystyrene. Different blend compositions of treated waste natural rubber latex (TWL) and PS were carried out through solution blending. Tensile and tear properties were investigated. The compatibility improvement of the 70/30 TWL/PS blends was further investigated using styrene butadiene rubber (SBR) and styrene graft natural rubber (SNR) as compatibilizer. The mechanical properties for TWL/PS blends were improved at 15 phr of SNR.

Key words: latex waste, solution blending, compatibilizer, SNR, SBR.

1. Introduction

Thermoplastic elastomers (TPEs) are materials that combine both thermoplastic and elastomeric properties (Rajalekshmi and Joseph, 2005; Asaletha et al., 1999; Ismail and Suryadiansyah, 2002; Nevatia et al., 2002; Joseph and Thomas, 2003). They behave as a vulcanized elastomer but can be melted at high temperatures (Aoyama et al., 1999; Chatterjee and Naskar, 2007). TPEs contain soft segments in the elastomer phase and hard segments in the thermoplastic phase. Recently, thermoplastic elastomers have been used to replace rubber in many applications. There are many methods for preparing the TPE, with blending as a common method normally applied.

In recent years, the development of TPEs from blends of polystyrene (PS) and natural rubber (NR) has become very attractive due to high modulus, rigidity, and low cost of PS as well as the good elasticity and good abrasion resistance of NR. Asaletha et al. (1999) showed that blends of polystyrene and natural rubber depends on the processing condition, i.e. samples from different mixing methods; melt mixing, and solution casting will give different properties. By comparing melt mixing method with different crosslink systems using sulfur, peroxide, and mixed system, they found that the morphology and crosslink density of the TPVs cured with different vulcanizing systems has influenced the mechanical properties of the blends.

Recently, due to environmental awareness and the necessity for greater cost efficiency, various researchers (Nevatia et al., 2002; Ismail and Awang, 2008; Jose et al., 2010; Noriman et al., 2010; Bazhenov et al., 2006) have addressed the usage of waste or recycle materials which include waste latex. The waste latex is an interesting material because it contain about 95% of high quality rubber hydrocarbon which is lightly crosslinked (Mathew et al., 2001). Previous researchers have showed that waste latex rubber
Preparation of treated natural rubber latex waste

2.1 Materials

Polystyrene (PS) was obtained from Total Petrochemical. Natural rubber latex (NRL, 61.61% dry rubber content) was supplied by ZARM Scientific & Supplies (Malaysia) Sdn. Bhd. Natural rubber latex waste (WL) was collected from the latex laboratory of the School of Materials and Mineral Resource Engineering at Universiti Sains Malaysia. Styrene graft natural rubber (SNR) was prepared referring to work by Tho (Tho, 2000). Deproteinized natural rubber (DPNR) was obtained from Sumirubber Industries (M) Sdn. Bhd. (Sungai Petani, Malaysia). Styrene monomer was purchased from Fluka Chemical Company (M) Sdn. Bhd. (Kuala Lumpur, Malaysia). Ammonium persulfate (NH4)2S2O8 was supplied by Fluka Chemical Company (M) Sdn. Bhd. (Kuala Lumpur, Malaysia). Styrene butadiene rubber (SBR) was obtained from Bayer (M) Co., Ltd and chloroform was supplied by Merck Sdn. Bhd.

2.2 Preparation of styrene graft natural rubber

Styrene graft natural rubber (SNR) was prepared using DPNR latex and placed into the reaction vessel, followed by distilled water. Then, it was heated in a water bath at the temperature of 60°C. The system was stirred at a speed of 200 rpm, and the initiator (NH4)2S2O8 was added to the system. The styrene monomer was fed into the system by dropping using a separating funnel. After completion of monomer addition, the time was recorded, and the system was continuously stirred for 5 hrs. It was then left at ambient temperature for 24 hrs before further use as a compatibilizer.

2.3 Preparation of treated natural rubber latex waste

According to the preliminary experiment, natural rubber latex waste (WL) without treatment and polystyrene blend cannot give good continuous films. Thus WL was treated with 20% by dry weight of natural rubber latex (20 g of dry NRL, 80 g of dry WL) referring to work by Rajalekshmi (2005) without curative. The treatment was done before blending with polystyrene. WL was heated in water bath at temperature of 50°C and stirred with a mechanical stirrer for 5 minutes at a constant speed of 300 rpm. Then, NRL was added and continued stirred for 20 minutes. The treated waste natural rubber latex (TWL) was kept at ambient temperature for 24 hrs before further use.

2.4 Preparation of blend

The PS was dissolved in chloroform prior to addition of TWL (5% (w/v)). The mixture was soaked for 24 hrs and stirred at a speed of 800 rpm for 7 hrs using a mechanical stirrer. The blends were stirred continuously for 8 hrs at a speed of 200 rpm to reduce the formation of bubbles. Solution blend compositions of 100/0, 70/30, 50/50, 30/70 and 0/100 were casted on a glass plate and dried for 3 days at 70°C in an oven. The 70/30 of TWL/PS blend was used to investigate the effect of the compatibilizer. Different loadings (5, 10, 15, and 20 phr) of styrene butadiene rubber (SBR) and styrene graft natural rubber (SNR) were applied. The compatibilizer was added after the mixture of TWL and PS was completely dissolved.
3. Characterization

3.1 Characterization of SNR

The grafting efficiency of SNR which was prepared by in-situ polymerization as explained in Section 2.2 was carried out. SNR was cast on a glass plate and dried at room temperature. After that, the SNR film was extracted the ungraft-NR and ungraft-PS using petroleum ether and mix of methyl ethyl ketone (MEK)/acetone, respectively (Arayapranee and Rempel, 2008). The residue SNR film was dried in an oven at 50°C until constant weight was achieved. The grafting efficiency was calculated as follows:

\[ \% \text{grafting} = \frac{\text{mass of extract (g)}}{\text{mass of specimen used (g)}} \times 100 \]

The residue SNR was also evaluated in terms of the function group using FTIR Perkin-Elmer Spectrum One Series spectrometer and was scanned in range of wavelength from 400 cm\(^{-1}\) to 4,000 cm\(^{-1}\).

3.2 Mechanical properties

A tensile test was done according to the ASTM D 412 test method with a cross-head speed 500 mm/min using an Instron universal machine model 3366. A tear test was conducted according to ASTM D 624 with a cross-speed of 500 mm/min of Instron universal machine model 3366. The test pieces were prepared from the casted films and the results presented were average from five samples.

3.3 Scanning electron microscopy analysis

Morphological studies of casted films were carried out using a scanning electron microscope (SEM; ZEISS Supra 35 VP). The samples were sputter-coated with a thin gold layer to avoid any electrostatic charge prior to scanning.

3.4 Thermogravimetric analysis

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were performed using a DTG-60H, simultaneous DTG-TG apparatus (shimadzu). The sample of 6-10 mg was put in aluminum pans and heated from 30 to 600°C at a rate of 10°C/min.

4. Results and Discussion

4.1 NRL/PS and TWL/PS blends

4.1.1 Mechanical properties

Figure 1 shows the mechanical properties of the NRL/PS and TWL/PS blends prepared from the solution casting. Comparing of NRL and TWL, the tensile strength (TS) of TWL is higher due to the crosslinked molecules (TWL is from WL, compounds used in the dipping process). It is well known that crosslinks can improve the material strength (Asaletha et al., 1999; Rooj et al., 2011); thus, it is not surprising that TWL shows higher TS than NRL, which is without crosslinks. When NRL was blended with PS (NRL/
PS), it showed a slight increase of TS with addition of 30% PS (70/30 NRL/PS) and then again a significant increase at 50% PS (50/50 NR/PS). This indicates that PS behaves as reinforcement in the NRL matrix phase due to its rigidity. Interestingly, TS decreased when the blend contained 70% PS (30/70 NRL/PS). This could be attributed to the phase inversion which takes place between 50% PS (50/50 NRL/PS) to 70% PS (30/70 NRL/PS). In intermediate stage, the disperse phase is change to be matrix phase; thus, many large phase boundaries were presented as weak points in the blend and resulted in decreased of tensile strength which show in NRL/PS solution blend. However, the TS are expected to increase again when the PS act as the matrix phase and will increase when the PS content increases, which insinuated the highest TS at PS film. Similar to Asaleta et al.’s findings (Asaletha et al., 1999), every solution casting blend (based on chloroform, benzene and carbon tetrachloride) showed a TS drop and then raised again at the point at which phase inversion is possible.

For the TWL/PS blends, TS also increased with the addition of 30% PS into TWL due to the reinforcement. In this case, TS dropped from the 30% PS (70/30 TWL/PS) to the 50% (50/50 TWL/PS) and then slightly increased again with addition of 70% PS (30/70 TWL/PS); it shows the highest value for the 0/100 sample (PS casted film). The phase inversion of TWL/PS blends occurred in between these compositions, where the PS content is lower compared to the NRL/PS blend. This is attributed to the crosslinks in TWL (crosslink density of 3.08x10^{-5} g-mol/cm^3). The crosslinked molecules naturally have high surface tension in their own network phase, where the volume sizes are smaller than in the uncrosslinked material. Thus, the phase inversion of TWL occurred at lower PS content compared to NRL/PS blend.

For elongation at break (EB), it was found that NRL gave a higher EB than TWL. This contributed from NRL, which is a noncrosslinked material, so the molecule chains slip past other molecule chains and move more easily compared to TWL, which is a crosslinked material. The EB of the NRL/PS blend decreased when the PS content increased due to the rigidity of PS in those blends. The observation is similar to the trend in TWL/PS blends.

The modulus at 100% elongation (M100) of blends is shown in Figure 1(c). The M100 of the NRL/PS blends increased with increasing PS content. This is because PS resists the mobility of rubber chains, which increases blend stiffness. No M100 was recorded in the 30/70 and 0/100 NRL/PS, because the sample could not extend to 100%. In the case of TWL/PS blends, 30% PS was added to TWL and resulted in significant improvement of M100. No M100 recorded for blends with 50% and 70% PS due to the stiffness of sample which could not reach 100% elongation.

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Figure 2 presents the tear strength of the blends. The tear strength of TWL is higher than NRL, probable due to the presence of crosslinks, which resists crack propagation (Agarwal et al., 2005). In the case of NRL/PS blends, the tear strength improved when the PS content increased, because

4.1.2 SEM analysis

Scanning electron micrographs of solution casted NRL/PS and TWL/PS blends are shown in Figure 3 and 4. Figure 3 shows that the rubber particles are round shaped
and PS are flake shaped, and the amount of rubber particles increases as the rubber proportion increased. For the morphology of the 30/70 and 50/50 TWL/PS the PS region formed a wall structure as shown in Figure 4(a) and (b). This is because TWL contains crosslinked molecules, which have high surface tension in their own network (Fukahori, 2010). It hardly entangles with other polymer chains and after the mixing process the network molecules and other polymers can be easily distinguished. Hence, the TWL and PS phases are clearly separated at composition of 30/70 and 50/50 TWL/PS, which causes poor interfacial interaction between the phases and gave much lower tensile and tear strengths compared to NRL/PS at similar compositions. However, 70/30 TWL/PS showed better morphology without the phase separation. It may due to PS, which dispersed in TWL at this composition. There is a possible limit in the dispersed amount of PS in TWL matrix; in case the amount of PS is higher, then it would form another region (PS wall in case of 30/70 and 50/50 TWL/PS). Moreover, 70/30 TWL/PS showed a smaller particle size compared to NRL/PS at any composition due to the fact that the NRL particle size is not stable and possible to combine with other particle after the mixing process due to uncrosslinking, hence NRL showed bigger particle sizes, which contribute to higher tensile and tear strengths. Based on the results, the 70/30 TWL/PS blend shows better tensile, tear and morphological properties compared to other composition; thus, it was selected for further studies.

4.2 Effect of compatibilizer

4.2.1 Characteristics of styrene graft natural rubber

The grafting efficiency of SNR prepared in this work is 77.2%. It is a little lower compared to the result in earlier research (79.1%) (Tho, 2000). Figure 5 shows FT-IR spectra of SNR compared to PS and NR. The SNR film was extracted by petroleum ether and a mix of MEK/acetone to remove ungrafted NR and PS, respectively. It also shows the characteristic bands of the aromatic group, -C=*=C at 1,496 cm\(^{-1}\) and -C=*=H at 698 cm\(^{-1}\), and it also shows -C=*=H of aliphatic (alkene) at 1,022 cm\(^{-1}\). Hence, it could be proved that PS was grafted on NR chains.

4.2.2 Mechanical properties

Figure 6 shows the relation between stress and strain from the tensile test of TWL/PS blends with different amount loadings of SNR and SBR. In case of SNR, blends with SNR at 5, 10, and 20 phr gave lower toughness (consider area curve) compared to the control sample (uncompatibilized); toughness improved only with 15 phr of SNR. The strength of the blend decreased with the addition of SNR at 5 and 10, increased at 15 phr, and then decreased at 20 phr. This may due to SNR was added as the elastomer in the blend; when the amount of elastomer increased, the strength decreased (Ong and Hashim, 2011). In addition, small amount of SNR as a compatibilizer to cover the blend particles; thus, those SNR behaved as weak points in this blend. However, when more amount of SNR was added at 10 phr, the strength and elongation increased from 5 phr SNR, but the values are still lower than in the control sample. After the amount of SNR increased to 15 phr, the results show a significant improvement of tensile strength and elongation. This reveals that the phase adhesion improved at 15 phr SNR. The excess SNR formed micelles in the matrix phase, which acted as defect points (Mathew and Thomas, 2003); the strength and elongation drastically decreased when the amount of SNR increased to 20 phr. Moreover, the water in SNR emulsion probably induced phase separation in the CHCl\(_3\) solution system for high amount of SNR, leading to poor mechanical properties (Chuayjuljit et al., 2005). For SBR, strength and elongation decreased when the amount loading of SBR increased. It is because SBR is a random copolymer that is difficult to locate between interfaces (Joseph et al., 2005). It might exist as a micelle and decrease mechanical properties. On the other hand, Joseph et al. (Joseph et al., 2002) reported that SBR is able to reduce...
the interfacial tension between PS/PB, which shows the reduction of die well; however, SBR may not efficient for solution blending systems.

Figure 7 shows the tear strength of the blends with different compatibilizer loadings. The addition of SNR in the blends improved tear strength significantly for 15 and 20 phr; lower amounts (5 and 10 phr) are slightly higher than the control sample. Phase adhesion increased; thus, crack propagation was obstructed. However, at high loading of SNR contribute to the excess of SNR which formed micelles, which decreased the tear strength for 20 phr from 15 phr SNR loading. In case of SBR, the tear strength increased for 5 phr; perhaps those SBR behave as the resistance of crack propagation; however, a higher amount loading of SBR presented weak points of blend.

4.2.3 SEM analysis

Figure 8 shows the morphologies of the TWL/PS blend with different loadings of compatibilizer. In the case of SBR, morphology improvement could not be achieved. The particle size of blends using a compatibilizer did not significantly differ from that of the uncompatibilized blend, as shown in Figure 7. The conformation of SBR is a random copolymer; as it could not be located at the interface between the TWL and PS phases it could not reduce the interfacial tension and stabilize the particle size. Moreover, it could potentially form micelles, which decrease the stress, elongation at break as shown in the stress-stain curve (Figure 6(b)) and also decrease tear strength (Figure 7) (Joseph et al., 2005).

The blend with 15 phr SNR shows the smallest particle size. The SNR could locate between interfaces and cover the particles to stabilize them. Those particles could not combine with other particles after mixing process (Robeson, 2007) hence the blend with 15 phr of SNR showed the smallest...

Figure 6. Stress-strain curves of (a) TWL/PS blend with SNR and (b) TWL/PS blend with SBR; (0, 5, 10, 15 and 20 phr).

Figure 7. Tear strength of TWL/PS with different loadings of SBR and SNR.

Figure 8. Morphology of TWL/PS with different amounts of compatibilizer (mag=1000).
particle size, which reduces the probability of phase separation for the sample under loading. Hence, it showed the highest stress and elongation at break as showed in stress-stain curve (Figure 6(a)) and highest tear strength (Figure 7) compared to SBR and other SNR loading.

4.2.4 Thermal properties

Figure 9 shows the TGA and DTG curves of blends with different amount loadings of SBR and SNR; Table 1 summaries the TGA and DTG results (first peak corresponding to rubber degradation and second peak corresponding to PS degradation). It does not show a significant difference of onset or degradation temperature of the blend with SNR. Thus, compatibilization using SNR does not improve the thermal stability of the blends. Because SNR comprises NR and PS molecules, which are the similar as the blend component, hence, its degradation temperature is also similar. Blends with high SBR show significantly higher degradation temperatures on 2nd peaks; in contrast, the onset temperatures of blends with any amount loading of SBR do not differ. Since SBR has higher degradation temperatures than rubber and PS (Varkey et al., 2000), it raises the degradation temperature of the blend.

The temperatures at 25%, 50% and 75% weight loss of TWL/PS blends are shown in Table 2. The temperature at 25% weight loss of the blend with SBR is slightly higher than the uncompatibilized blend and generally higher at 50% and 75% weight loss. The higher temperature with the addition of SBR indicates that SBR increases the thermal stability. This is probably because the stability temperature of SBR is higher than that of other components; hence, it contributes to higher degradation temperatures (Varkey et al., 2000). In the case of SNR, there are no significant differences in degradation temperature of the blends. This is because SNR is synthesized from NR and PS, so the degradation of both materials is similar and merged to those peaks of the blend components.

5. Conclusion

From the study, it can be concluded that waste natural rubber latex can be used to produce a value added product. The 70/30 TWL/PS blends showed better mechanical properties compared to other compositions. The compatibilization through addition of compatibilizer was studied; here good interfacial characteristics were obtained with the addition of 15 phr SNR. The mechanical properties improved, but thermal properties remained the same due to small loading of compatibilizer. The blend with a high amount of SBR resulted in small weight loss due to it is high thermal stability.

Acknowledgments

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References

Table 1. Onset and degradation temperatures of the TWL/PS blend with compatibilizer.

<table>
<thead>
<tr>
<th>Amount of compatibilizer (phr)</th>
<th>TGA onset</th>
<th>DTG 1st peak</th>
<th>DTG 2nd peak</th>
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<tr>
<td></td>
<td>SBR</td>
<td>SNR</td>
<td>SBR</td>
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<tr>
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<td>352.98</td>
<td>352.98</td>
<td>378.83</td>
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<tr>
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<td>379.72</td>
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<td>352.47</td>
<td>355.06</td>
<td>380.07</td>
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<tr>
<td>20</td>
<td>354.95</td>
<td>353.92</td>
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Table 2. Degradation temperatures at 25%, 50% and 75% weight loss of the TWL/PS blend with compatibilizer.

<table>
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<tr>
<th>Amount of compatibilizer (phr)</th>
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<th>50% weight loss(°C)</th>
<th>75% weight loss(°C)</th>
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<td>SNR</td>
<td>SBR</td>
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