ABSTRACT

Blends of poly(lactic acid) / epoxidized natural rubber (PLA/ENR) by melt compounding in twin screw extruder was studied. The 90/10 composition of the PLA/ENR blend gave the highest tensile strength, modulus and elongation at break as 18.34 MPa, 885.67 MPa and 2.86 % respectively; therefore, this composition was selected to be blended with organoclay. The addition of organoclay, twice-functionalized organoclay (TFC) and Cloisite® 25A (C25A) improved the tensile strength and modulus of the PLA/ENR blend because the organoclay acted as reinforcing agent. However, the addition of TFC greater improved tensile strength, modulus and elongation at break than that of C25A, especially at the TFC content of 5 and 7 wt%. This result suggested that the epoxy group grafted onto TFC helped increase the compatibility of ENR and PLA by interaction with the epoxide group and the hydroxyl group.

Key words: epoxidized natural rubber, poly(lactic acid), organoclay, nanocomposite, extrusion

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INTRODUCTION

poly(lactic acid) (PLA) is a biodegradable and thermoplastic derived from renewable resources, thus it is appropriate for packaging application. However, PLA is brittle, which limited its use. Blending PLA with rubber will improve toughness obviously.\textsuperscript{1,2} However, the blend deteriorate if the PLA and rubber pair is not compatible. Many researchers investigated the introduction of a block copolymer as a compatibilizer\textsuperscript{3-5} and the introduction of a nanoclay\textsuperscript{6,7} to improve miscibility of polymer blends. The additions of an organoclay improve material properties, resulting from the increased surface area between the polymer matrix and clay platelets. The interaction of polymer and the organoclay can generate a clay-polymer complex; therefore, exfoliation of the clay increases\textsuperscript{8} and the domain size of the immiscible blends became much smaller.\textsuperscript{9}

The compatibilization and the exfoliation require functionality of the two polymers and the clay. Natural rubber is non-polar, but epoxidized natural rubber (ENR), derived from the partial epoxidation of the natural rubber molecule is polar. The ENR, which has more polarity than natural rubber, became more compatible with the poly(lactic acid). The study showed the increase in impact strength, but decrease in strength and modulus of the PLA/ENR blend.\textsuperscript{2} The result indicated the need to introduce an organoclay for the ENR/PLA blend systems.

A good selection of organoclay is critical to the compatibilization of the polymer blend. An organoclay, Cloisite\textsuperscript{®} 25A (C25A), can be modified by the addition of epoxy groups to molecules. Epoxy groups were grafted to C25A by a treatment with a silane coupling agent to produce twice functionalized organoclay (TFC).\textsuperscript{10,11} The properties of polymer blend between PLA and ENR can be better improved by addition of TFC in comparison with that of C25A blend system. The main aim of this study was to examine the dispersion and the role of the organoclay in the immiscible polymer blend composed of poly(lactic acid) (PLA) and epoxidized natural rubber (ENR).

MATERIALS AND METHODS

Materials

PLA was purchased from Thantawan Industry Company Limited with a weight-average molecular weight of 2.4\times10^{5}. PLA was dried in a hot oven at 60 °C for 24 h. ENR was purchased from Muang Mai Guthie Public Co. Ltd. ENR had a weight-average molecular weight of 6.4\times10^{5}. The organoclay, Cloisite\textsuperscript{®} 25A (C25A), was purchased from Southern Clay Product Inc. The twice-functionalized organoclay (TFC) with the epoxy groups was prepared by treating the C25A with silane coupling agent.

Preparation of TFC

In order to modify C25A into TFC, a mixture included 3.5 g of the silane coupling agent and 200 mL of 90% ethanol solution was prepared. The 10 g of C25A was added. The C25A was soaked
in the acidic solution for 12 h at room temperature. The mixture was then heated at 70 °C. The clay was washed with ethanol at room temperature.

**Blending of nanocomposites**

Nanocomposites of PLA/ENR/organoclay were compounded in a twin-screw extruder. Barrel temperatures were 90-110, 150 and 200 °C at the feeding, transition and high pressure extrusion zones respectively with screw speed was 60 rpm. The extrudates were pelletized with 700 cycles per minute. PLA was blended with ENR at various compositions, 100/0, 90/10, 80/20, 70/30, 60/40, and 50/50. The C25A and TFC were mixed with the 90/10 PLA/ENR blend in the amount of 0, 1, 3, 5, and 7 wt% clay. Each compound was compressed by Kao Tieh Go Tech compression molding machine at 190 °C, held at pressure 15 MPa for 12 min, and cooled under the pressure for 3 min. Molded samples were cut into dumbbell shaped specimens according to ASTM D638 for tensile tests.

**Mechanical testing of blends**

Tensile testing was done according to ASTM D638, by an Instron testing machine. The crosshead speed was set at 50 mm/min. Impact testing was done according to ASTM D256 by using a pendulum impact tester.

**X-ray measurements**

X-ray measurements were carried out by using a XRD model JDX-8030 with reflection geometry and Cu KR radiation (wavelength λ = 0.154 nm) operated at 40 kV and 100 mA. The data were collected within the range of the scattering angles (2θ) of 2-30°.

**RESULTS AND DISCUSSIONS**

**Chemical modification of C25A**

![Figure 1. FTIR spectra of the Cloisite 25A. which was treated with a silane coupling agent for difference times: (a) 0 h and (e) 12 h. The inset displayed the IR spectra near the peak intensity of Si-OH stretching.](image-url)
The silane coupling agent was capable to react with a silanol group (Si-OH) resulted in the grafting of an epoxy functional group onto the C25A. This epoxy group would increase the interaction of the clay layer with PLA. The grafting of epoxy group by the silane coupling agent could be observed through the FTIR spectroscopy, near the intensity peak at 3636 cm\(^{-1}\), which was assigned to the stretching of Si-OH on the surface of C25A. Figure 1 shows the change in the Si-OH absorption peak of C25A. The Si-OH peak became smaller as the reaction progressed, which indicated the decrease in the amount of silanol group on C25A upon the length of the treatment time. This reduction of the Si-OH peak confirmed the chemical reaction between the silane coupling agent and the silanol groups on C25A, yielded TFC clay contained epoxy content.

**Mechanical properties of the blends**

The effect of PLA and ENR blending on the modulus, elongation at break, tensile strength, impact strength and hardness were shown in Table 1. As expected, the addition of ENR reduced the modulus and strength significantly, while improved the elongation at break. However, at the composition of ENR more than 10%, the elongation at break dropped dramatically, and so do the modulus and the tensile strength. The impact strength increased upon increasing the amount of ENR. However, the tensile properties of PLA/ENR composites were decreased as the loading of ENR increases. This may be attributed to the elastomeric behavior and compatibilisation effects of ENR. At 10% ENR or less, chemical interaction probably occurred between the oxirane group of ENR and the hydroxyl group in PLA. The chemical interactions between PLA and ENR were proposed in Figure 2. It was believed that the hydrogen bonding could form between the OH group of PLA and the exopoxide group of ENR. The results from the mechanical properties indicated that the 90/10 composition of the PLA/ENR blend had the highest modulus, elongation at break and tensile strength compared to other compositions. Thus, the PLA/ENR10 was selected for the further investigation of the effect of the modified organoclay. In order to improve toughness and strength to PLA, the ENR must be distributed as small domains (usually 0.1-1.0 µm) in the matrix PLA, and the ENR must have good interfacial adhesion to PLA.
Table 1. Tensile properties, impact strength and hardness of PLA/ENR binary blend.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Modulus (MPa) ± SD</th>
<th>Elongation at break (%) ± SD</th>
<th>Tensile strength (MPa) ± SD</th>
<th>Impact strength (KJ/m²) ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>1874.34 ± 1.62</td>
<td>2.26 ± 1.84</td>
<td>44.67 ± 1.62</td>
<td>3.33 ± 0.98</td>
</tr>
<tr>
<td>PLA(90)/ENR(10)</td>
<td>885.67 ± 1.08</td>
<td>2.86 ± 0.92</td>
<td>18.34 ± 1.62</td>
<td>5.56 ± 1.56</td>
</tr>
<tr>
<td>PLA(80)/ENR(20)</td>
<td>815.67 ± 1.15</td>
<td>0.93 ± 0.98</td>
<td>8.00 ± 0.56</td>
<td>4.40 ± 0.65</td>
</tr>
<tr>
<td>PLA(70)/ENR(30)</td>
<td>175.00 ± 0.98</td>
<td>0.70 ± 1.35</td>
<td>0.70 ± 0.26</td>
<td>4.50 ± 1.47</td>
</tr>
<tr>
<td>PLA(60)/ENR(40)</td>
<td>138.34 ± 1.82</td>
<td>0.75 ± 1.88</td>
<td>1.17 ± 0.73</td>
<td>10.80 ± 0.87</td>
</tr>
<tr>
<td>PLA(50)/ENR(50)</td>
<td>29.00 ± 1.41</td>
<td>0.70 ± 1.64</td>
<td>0.86 ± 0.11</td>
<td>10.30 ± 1.18</td>
</tr>
</tbody>
</table>

* PLA(90)/ENR(10) = PLA 90 parts and ENR 10 parts

Figure 2. Proposed chemical interactions between PLA and ENR

Mechanical properties of PLA/ENR/organoclay composites.

The PLA(90)/ENR(10) blend was subjected to be mixed with an organoclay in order to find the optimum compatibilization of the blend, which the mechanical properties were the highest. The tensile strength (a), modulus (b) and elongation at break (c) of PLA/ENR/TFC and PLA/ENR/C25A composites were plotted in Figure 3 for various contents of TFC and C25A. The tensile strength did not observe much difference between C25A and TFC when the amount of clay less than 3 wt%. Significant improvement occurred when the amount of TFC was more than 3 wt%. Because of there are more enough epoxy content to react with OH group of PLA. The addition of both clays gave an increase in tensile strength although the TFC was better. Figure 3(b) represents the modulus of nanocomposites. The modulus improved significantly upon adding both C25A and TFC to PLA(90)/ENR(10) blend. Overall, TFC gave a better enhancement on modulus than C25A. The
significant increase of modulus was undeniably due to the contribution from clays. Not only the clays acted as a reinforcing agent, but also performed as a compatibilizer as seen from Figure 3. The increase in modulus was not monotonic. Nevertheless, the 1 wt% of clay yielded the highest modulus of all the tested clay compositions. Figure 3 (c) displayed the elongation at break of PLA/ENR/C25A and PLA/ENR/TFC composites. The addition of C25A and TFC reduced the elongation at break of PLA(90)/ENR(10). It was also found by Chen et al.\textsuperscript{13} that the increase in the modulus of the polymer-clay composites would result in a reduction in the elongation at break, because of the improvement in strength. When the clay composition was higher than 3 wt%, the elongation at break of the PLA/ENR/TFC composite started to gain compared to the PLA/ENR/C25A composite. Evidently at 5 wt% of TFC, the compatibilization and the exfoliation of TFC became effective. It was believed that the significant enhancement of TFC to the mechanical properties associated with the epoxy groups on TFC, which endorsed an interaction between TFC and PLA via a chemical interaction between epoxy groups of the TFC and the end groups of PLA.

The C25A slightly improved tensile strength and modulus but not as much as TFC. That was because TFC contained grafted epoxy group which had a stronger interaction to PLA than that of the silanol group in C25A.

![Graphs](image-url)

**Figure 3.** Tensile strength (a) Modulus (b) and Elongation at break (c) of PLA/ENR (90/10) with various contents of C25A and TFC.
X-ray diffraction measurements

The structure of the character organoclay and the polymer blend with organoclay were investigated by XRD as shown in Figure 4. Figure 4 shows XRD patterns of PLA(90)/ENR(10), C25A, TFC, PLA/ENR/TFC and PLA/ENR/C25A composites. The PLA(90)/ENR(10) (Figure 4 (A)) without clay exhibited its \(d_{001}\) spacing of 9.35 Å. Whereas Figure 4 (B) shows \(d_{001}\) spacing of TFC dispersed in PLA/ENR blend as 32.70 Å, 32.65 Å, 33.14 Å and 33.70 Å for 1, 3, 5 and 7 wt% respectively. The characteristic peak of TFC shifted to lower 2\(\theta\) after compounding with PLA/ENR. This reveals that the layer expansion by polymer intercalation. The increase in the d-spacing of the composites indicate that the polymer molecules were inserted into the interlayer of organoclay leading to improvement of composite’s mechanical properties. Figure 4 (C) shows \(d_{001}\) spacing of the PLA(90)/ENR(10) / C25A as 32.91 Å, 32.59 Å, 32.99 Å and 32.98 Å for clay loading 1, 3, 5 and 7 wt% respectively. Moreover, the higher degree of basal spacing expansion of PLA/ENR/TFC compared to PLA/ENR/C25A usually results in the higher chance of polymer intercalation.¹⁴

![Figure 4](image-url)

**Figure 4.** XRD patterns of: (A) PLA(90)/ENR(10), C25A and TFC, (B) and (C) PLA/ENR/TFC and C25A with the following wt% compositions.
Figure 5. Typical TEM photographs of PLA/ENR/C25A (a and b) and PLA/ENR/TFC (c and d) with clay loading of 5 wt%. Each left photograph is at low magnification (scale bar: 0.5 µm), and right photograph is at high magnification (scale bar: 100 nm).

Figure 5 (a and b) shows typical TEM micrographs of the PLA/ENR/C25A with clay loading 5 wt% and Figure 5 (c and d) shows that of PLA/ENR/TFC with the same clay loading 5wt%. In these TEM photographs, the light regions and dark bands represent the PLA and the ENR, respectively. The dark lines correspond to the cross section of the clay sheets that have been delaminated and dispersed in polymer blend. Higher degree of dispersed of the silicate layers was obtained for the PLA/ENR/TFC composite than for the PLA/ENR/C25A. These results were in agreement with XRD results previously. It can conclude that dispersion of clay in polymer blend is good.

CONCLUSIONS

Brittle PLA was blended with epoxidized natural rubber (ENR) with an aim to increase ductility of PLA. However, the blend greatly sacrificed the modulus and tensile strength. A functionalized clay should be added to increase the compatibilization of PLA and ENR, thus, improved the tensile strength and modulus without the drop in the elongation at break. The 90/10 composition of the PLA/ENR blend gave the highest elongation at break; therefore, the composition was blended with organoclay to obtain the highest properties of the composite. C25A clay was modified by exchanging
of silanol group for epoxy group, by treated C25A with a silane coupling agent to produce the twice-functionalized organoclay (TFC). The addition of both TFC and C25A improved the tensile strength and modulus of the PLA(90)/ENR(10) blend. That was because the clay acted as reinforce agent. However, the introduction of TFC greater improved strength, modulus and elongation at break than C25A, especially when the clay of 5 and 7 wt%. The composite that had the high modulus, the highest strength, and a reasonable elongation at break was produced from 90/10 PLA/ENR blend, which contained 7 wt% of TFC. This result suggested that the epoxy group grafted onto TFC helped increase the interaction of TFC to ENR and PLA. The epoxy groups on the TFC surface stimulated the exfoliation of the clay and the compatibilization of PLA and ENR.

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REFERENCES


