Toughening Effect of Clay Particles on Poly(Lactic Acid)/Natural Rubber Blend

Jung Hyun Ahn, Joung Sook Hong*, †, and Kyung Hyun Ahn*

School of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University, Seoul 08826, Korea
(Received : December 27, 2019)

In this study, the effect of clay particles on toughening behavior of poly(lactic acid) (PLA)/natural rubber (NR) blend is investigated. PLA and NR were blended in various compositions (70/30, 60/40 and 50/50 PLA/NR) with two types of clay, organoclay and natural clay (Montmorillonite). Linear viscoelasticity analysis and morphology observation of the blends were carried out to investigate change in the blend morphology in the presence of clay. As the NR content increases from 30 wt% to 50 wt%, the NR domains coarsens, changing the blend morphology from droplet to apparent co-continuous structure. With the change in the blend morphology, tensile behavior of the blend including tensile strength and elongation at break differs. Besides, the addition of clay to the blend affects the blend morphology in different way, especially depending on the localization and the clay content. Natural clay localized in the PLA phase induces coalescence of the NR droplets while organoclay reduces the NR drop size due to interfacial localization of clays in the PLA/NR blend. For the droplet morphology, toughening behavior of the PLA/NR blend improves (~ 60% elongation at break of 70/30 PLA/NR blend) only when a small amount of organoclay (0.5 wt%) is added. On the other hand, the 50/50 PLA/NR blend with the apparent co-continuous morphology improves the elongation at break as clay content increases regardless of the type of clay.

Key Words: Clay / Poly (lactic acid) / Morphology / Rheology / Toughening

1. INTRODUCTION

Poly(lactic acid) (PLA) is one of biopolymers that have high potential for industrial application due to its biodegradability, biocompatibility and processibility. However, it is brittle, restricting the applications of PLA. In order to overcome a drawback of brittleness and to induce toughening, many researches have been performed, especially by blending of brittle PLA with ductile polymer or elastomer. As tensile mechanical properties of polymer blend are changed depending on blend morphology, it is important to figure out the relationship between blend morphology and toughening of PLA. Toughening mechanism differs for droplet and co-continuous morphology. In the case of a droplet morphology, interfacial adhesion between two polymers determines whether debonding occurs at the interface or not. For a co-continuous morphology, not only the debonding process at the interface is involved in toughening, but also crack propagation within both two polymer phases is involved. So, it is important to understand the blend morphology and find the structure of the blend to induce toughening of PLA.

Among various candidates for the partner polymer of PLA, natural rubber (NR) is an attractive secondary phase since it is naturally abundant and environmentally friendly. Previous studies showed that there exist an optimal diameter of the dispersed phase and the distance between the dispersed NR domains to induce toughening to PLA with NR. In detail, a maximum strain reaches 200% with 1.1 – 2 μm diameter of NR when the rubber is mixed 10 wt%. Besides, co-continuous structure of the blend brings maximized ductility of the blend. Also, the PLA/NR blend forms co-continuous structure with 500 J/m of impact strength when NR is introduced 35 wt%. But the simple blending of PLA and NR is insufficient to toughen PLA and still, the optimal morphology of the PLA/NR blend is controversial.

Toughness of a polymer is the energy absorbed by the material during the deformation before failure. During tensile or fracture deformation of the polymer blend, debonding at the interface of the blend, cavitation of a secondary polymer, multiple crazing and shear-yielding process are involved. Although the role of the matrix is critical for absorbing energy under deformation, additional energy dissipation can be induced through debonding at the interface between the two polymers and cavitation of a secondary polymer. But most polymers are immiscible, so the given
deformation easily induces debonding at the blend interface. And the cavities merge each other, leading to quick failure under the deformation\(^{11, 12}\).

At this point, particles have been used for additional control of the morphology of the polymer blend\(^{13, 14}\). Inorganic or organic particles are introduced to control the interaction between polymers. Depending on localization and self-assembled structure of particles, the blend ductility is changed significantly\(^{7, 11, 12}\). Also particles can change the shape of the dispersed phase. So it is essential to understand the morphology of the blend with particles. For a fundamental understanding of toughening effect of particle, clay particle, as one of the most useful mineral particles for polymer composite product is investigated for the toughening of the PLA/NR blend in this study. Clay not only can improve mechanical performance of PLA, but also induce barrier performance against water depending on degree of dispersion.

In this study, the PLA/NR blend was mixed with clay particles (Montmorillonite) of two different types. Structure of the blend with particles are studied based on morphology observation and rheology analysis in order to understand toughening effect of clay particles, especially by comparing of the blend with natural clay (CNa\(^+\)) with that with organically modified clay (C20A). Specific structure of cation for both types of clays are shown in Table I.

### 2. EXPERIMENTAL

#### 2.1 Materials

The polymers used in this research were poly (lactic acid), PLA (4032D, Natureworks Co. LTD, USA) and natural rubber (CSR-5, CRK, South Korea). For additional toughening, clay fillers were introduced. In this study, two types of clay particles were used. One is natural clay, CNa\(^+\) (Cloisite Na\(^+\), BYK Additives, USA) with Na\(^+\) cation between interlayers and the other is organically modified clay, C20A (Cloisite C20A, BYK Additives, Germany). Specific structure of cation for both types of clays are shown in Table I.

#### 2.2 Preparation of blend

PLA and clay particles were dried in a vacuum oven for at least 8 h at 80 °C. Melt compounding was conducted through an intensive mixer (Rheocomp mixer 600, MKE, Korea) for 7 min at 200 °C. All the samples went through one step mixing, which means PLA, NR and clay particles were all put together at once. After mixing, chunks of the sample were molded to disk- and dog bone shape at 200 °C for 6 min using a hot press (CH4386, Carver) for rheological and mechanical property measurements. After molding, they were gradually cooled down at room temperature.

### 2.3 Characterization

For small amplitude oscillatory shear flow, a strain-controlled type rheometer (RMS 800, Rheometrics, USA) was utilized. Samples were prepared with a diameter and thickness of 25 and 0.45 mm, respectively. Rheology test was conducted under 190 °C. Before the test (dynamic frequency sweep test), all the samples went through 5 min of equilibration time after loading the samples into the rheometer. Uniaxial tensile test was conducted following the ASTM D638 type V with UTM (LF plus, Lloyd instruments Ltd). For each specimen, this test were repeated at least 7 times and the data were averaged with the standard deviation.

#### 2.4 Observation

Morphology of the blend was observed through scanning electron microscope (SUPRA 55VP, Carl Zeiss) under 2 kV. For the observation, cross section of the samples was prepared through cry-fracture process using liquid nitrogen and the sections were Pt-coated.

### 3. RESULTS AND DISCUSSION

This study investigates how clay particle affects the structure of the PLA/NR blend as well as tensile mechanical performance depending on the type of clay and concentration of NR. First of all, the tensile behavior of the PLA/NR blend is studied depending on the NR content without the addition of clay particles.

Figure 1 (a) shows tensile strength and elongation at break of neat PLA and PLA/NR blends. Mechanical properties were measured through UTM following ASTM D638
type V. For PLA, its tensile strength is 63.6 MPa and elongation at break point is 18.8%. When PLA is mixed with NR, the PLA/NR blend increases the elongation at break of the samples as shown in Fig. 1. However, it differs depending on the NR content. PLA/NR 70/30 blend shows 50% of elongation at break in average which is the highest among three PLA/NR blends, 70/30, 60/40 and 50/50 (w/w). Also it shows a whitening neck as indicated in Fig. 1 (b). As the NR content increases, ductility decreases different from expectation. It is attributed to dramatic change in morphology of the PLA/NR blend.

Figure 2 shows structural change of PLA/NR blend under particle introduction. From the SEM images of first column in Fig. 2, as NR content increases, PLA/NR blend looks phase separation from a droplet morphology. PLA/NR 70/30 shows the droplet morphology. A drop size is quite heterogeneous. PLA/NR 60/40 shows irregular shape of natural rubber and as PLA and NR were blended 50/50, NR formed huge phase along with PLA. Unlike the case of PLA/NR 70/30 blend where the NR domains are dispersed as a minor phase, it is difficult to distinguish which is the matrix or the dispersed phase in the case of PLA/NR 50/50, which means this composition is approaching the point where phase inversion occurs. According to the literature, a phase inversion occurs when \( \eta_d/\eta_m = \phi_d/\phi_m \) is equal to 15-17) (\( \eta_d \) and \( \phi_d \) are viscosity and volume fraction of the dispersed phase respectively, while \( \eta_m \) and \( \phi_m \) are viscosity and volume fraction of the matrix phase respectively). Using the complex viscosity for neat PLA and natural rubber respectively, viscosity ratio (\( p = \eta_{NR}/\eta_{PLA} \)) is approximately 2.15 (complex viscosities for PLA and NR are 1190 Pa·s and 2560 Pa·s at 190 ºC respectively at 100 rpm = 10.5 rad/s13)). It indicates that when the volume ratio of NR (\( \phi_{NR} \)) is 0.68 (weight ratio is 0.63 since density of polyisoprene is 0.93 kg/m³), phase inversion occurs. This is quite consistent with the SEM images of PLA/NR 50/50 blend (Fig. 2) where NR forms continuous phase over PLA. Role of organoclay is dramatically presented in the second column of Fig. 2. When 2 wt% of C20A was introduced, the morphology of PLA/NR blends is significantly changed as shown in Fig. 2. It is difficult to distinguish the NR droplets from the PLA matrix15, 21). The addition of C20A particles induces a significant decrease in the NR droplet size due to suppression of coalescence between NR droplets during the mixing process13, 14). The third column of Fig. 2 shows PLA/NR blend with 2 wt% of CNa⁺. The NR domains were coarsened after the addition of CNa⁺ particles, and this particle-induced coalescence is noticeable. Unlike C20A
which is known to be intercalated within the PLA/NR blend\textsuperscript{21}, CNa\textsuperscript{+} particles exist in agglomerates within PLA/NR blend. Different morphological change induced by two clays can be explained by their dispersion, localization in PLA/NR blend and viscosity ratio of the blend. From Table I, C20A has a larger d-spacing between the layers and ease to intercalate in hydrophobic polymer. Meanwhile, interlayers of CNa\textsuperscript{+} are tightly bonded with smaller d-spacing compared to C20A. Due to higher extent of dispersion of C20A than CNa\textsuperscript{+}, C20A particles easily form a particle dispersion structure with a small amount of clay and can induce a change in the blend morphology.

Table II Wetting coefficient and prediction of localization of clay in the PLA/NR blend.

| Types of clay | Wetting coefficient, $\omega$\textsubscript{particle} by Harmonic-mean eq (3) | Wetting coefficient, $\omega$\textsubscript{particle} by Geometric-mean eq (4) | Localization of clay |
|--------------|---------------------------------|---------------------------------|---------------------|
| CNa\textsuperscript{+}      | -2.48                           | -3.00                           | PLA phase           |
| C20A          | -1.13                           | -1.40                           | PLA phase or interface |

For PLA, NR, C20A and CNa\textsuperscript{+}, Surface energy of 200 °C is used from literature\textsuperscript{11, 18-21}.

From Fig. 2, the localization of clay particles is quite different from each other. Rather than directly observing where the clay particles are located in the blend, their localization can be predicted using wetting coefficient. Wetting coefficient of a particle ($\omega$\textsubscript{particle}) is defined\textsuperscript{11, 20},

$$\omega_{\text{particle}} = \frac{\gamma_{a-b} \text{ Harmonic-mean eq (3)}}{\gamma_{a-b} \text{ Geometric-mean eq (4)}}$$  

(1)

where $\gamma_{a-b}$ is an interfacial energy between component a and b. If the coefficient is over 1, the particle will be favorably located in NR. If it is below −1, the particle will be located in the PLA phase. When the wetting coefficient is between −1 and 1, particles will be preferentially placed at the interface between PLA and NR. The $\gamma_{a-b}$ is calculated in two ways, harmonic-mean and geometric-average of surface energy\textsuperscript{16, 19, 22}, which consists of dispersive part, $\gamma^d$ and polar part, $\gamma^p$. So, surface energy of a component is defined as

$$\gamma = \gamma^d + \gamma^p$$  

(2)

Interfacial energy between a and b components can be calculated using harmonic-mean equation:

$$\gamma_{ab} = \gamma + \gamma_b - 2 \sqrt{\frac{\gamma^d_b}{\gamma^d + \gamma^b} + \frac{\gamma^p_b}{\gamma^p + \gamma^b}}$$  

(3)

and geometric-mean equation:

$$\gamma_{ab} = \gamma + \gamma_b - 2 \sqrt{\frac{\gamma^d_b}{\gamma^d + \gamma^b} + \frac{\gamma^p_b}{\gamma^p + \gamma^b}}$$  

(4)

The harmonic mean equation (eq. (3)) is known to be valid to predict interfacial energy between low-energy components while geometric mean equation (eq. (4)) is to be valid between low energy component and a high energy component (higher than 20 mN/m)\textsuperscript{23, 24}. Since relative difference between the surface energy for each component (PLA, NR) is quite different from each other ($\gamma_{PLA}$ is 26 mN/m, $\gamma_{NR}$ is 15.55 mN/m, $\gamma_{C20A}$ is 25.44 mN/m and $\gamma_{CNa^+}$ is 44 mN/m\textsuperscript{2, 11, 18, 21}), interfacial energy was calculated through both two equations in order to get the reasonable predictions. Table II shows prediction of localization of clay particles in the blend according to $\omega$\textsubscript{particle}. According to the wetting coefficient from both equations (3, 4), CNa\textsuperscript{+} in the PLA/NR blend is predicted to be localized in PLA phase, while C20A is to be located near the interface of PLA/NR because $\omega_{\text{C20A}}$ has a value close to −1. For C20A particles, they are expected to act as a barrier between NR droplets during the mixing process. It means that C20A particles at the interface hinder NR droplet’s coalescence, leading to be compatibilized morphology as shown in the second column in Fig. 2. Though C20A particles are to be located near the interface, C20A particles also can be in the PLA phase from Table II. When C20A particles are solely dispersed within PLA, C20A increases the viscosity of PLA. For instance, when 3 wt% of C20A is dispersed at the PLA matrix, the complex viscosity of PLA/C20A at 0.1 rad/s rises from 1440 Pa·s to 9260 Pa·s. So it delays for the NR droplet to diffuse and even the volume fraction of the dispersed phase ($\phi_{NR}$) for phase inversion ($\phi_{NR} = 1/(1 + (1/p))$) is expected to decrease due to the decrease in the viscosity ratio (p) as long as C20A remains in the PLA phase. However, it is difficult to neglect that the viscosity increase of the PLA matrix with C20A particles decreases the chance of coalescence between NR droplets.

Figure 3 plots the storage and loss modulus as a function of frequency for the binary and the ternary blends under the linear viscoelastic region. Such a complex effect of C20A is also reflected on Fig. 3 with the increase of $G'$, $G''$ for the PLA/NR 70/30. For CNa\textsuperscript{+}, particles barely increase $G'$ and $G''$ of the blend compared to the neat PLA, which rather leads to increase in viscosity ratio (p). When CNa\textsuperscript{+} is mixed with PLA, the complex viscosity of PLA/CNa\textsuperscript{+} composite decreases. For example, when 3 wt% of CNa\textsuperscript{+} is added to PLA, the complex viscosity slightly decreases from 1440 Pa·s to 1360 Pa·s at 0.1 rad/s. This might be due to degradation of PLA itself when agglomerates of natural clay were mixed.
with PLA. For the PLA/NR 50/50 blend, the addition of CNa$^+$ changes the G’ and G” depending on the concentration of particle. With 2 wt% of CNa$^+$ both of G’ and G” decrease over the 0.1 rad/s −100 rad/s frequency range. Less viscous matrix makes it easier for the NR droplets to move around and collide each other. Also CNa$^+$ particle agglomerates are located in the PLA phase different from C20A at the interface, which means CNa$^+$ does not interrupt coalescence of NR phases. In this case of PLA/NR 50/50, the effect of C20A particles is less noticeable, the level of G’ decreases due to significant contribution of the NR phase since the NR phase is about to be the comparable component with PLA. From morphological and rheological analysis, two different clay play a different role for the PLA/NR blend due to different localization and degree of dispersion. In addition, the PLA/NR blend shows significantly different morphology from droplet to pseudo co-continuous, depending on the NR content. For those systems, their mechanical performance is investigated by comparison between blend with a small amount of clay particle (0.5 wt%) and that with 2 wt% because the blend shows significantly different rheology behavior with the smaller content of clay than 2 wt%.

Figure 4 (a) compares G’ and G” of the PLA/NR 70/30 blend at 0.1 rad/s as a function of clay content for both types. For C20A, 0.5 wt% of the particles induces an increase of G’ and G”. With 2 wt% of C20A, G’ exceeds G” which indicates that as C20A particles’ content increases, more interface between PLA and NR is created. Also the elasticity increase of PLA itself by dispersion of the higher amount of C20A in PLA contributes to the increase in storage and loss modulus. For CNa$^+$, the addition of particles slightly decreases G’ and G” compared to the neat blend when 0.5 wt% and 2 wt% of the particles is mixed. This might be due to the fact that the CNa$^+$ particles lower G’ of PLA. For the PLA/NR 70/30 as well as PLA/NR 50/50 blend, 0.5 wt% or 2 wt% of particles is added. Tensile performances of the blends are compared in Fig. 4(b) and (c). As shown in Fig. 4(b) and (c), the effect of clay particle on mechanical performance is significantly depending on the blend morphology and the content of clay. Additional toughening effect of clay particles was distinguished from that by the addition of NR. As the clay content differs, toughening effect differs. For 70/30 PLA/NR blend, the addition of NR to PLA improves the elongation at break, plus the addition of a small amount of C20A (0.5 wt%) improves further the elongation at break to 60%, while the addition of CNa$^+$ decreases the elongation at break (Fig. 4(b)). The addition of C20A particles to the PLA/NR 70/30 blend induces a significant decrease in the NR droplet size, resulting in the decrease of distance between NR droplets. It has been known that the decrease of distance between rubber particles toughens polymer/rubber blends by promoting the energy dissipation of the matrix$^{10}$. Besides, 0.5 wt% of C20A particles expects to be localized at the interface$^{13,14}$ and hold PLA and NR interface, which induces higher energy dissipation through debonding at PLA/NR interface compared to the
PLA/NR 70/30 blend without clay particles at the interface. With the higher content of clay (2 wt%), both clay decrease the elongation at break of the blend. Excess C20A particles are dispersed in the PLA matrix when C20A localizes sufficiently at the interface. They are reacted as stress concentration under the tensile deformation, which results in brittle tensile properties of the blend\(^{21}\). It means that there is an optimal content for C20A in order to induce higher ductility to the blend. On the other hand, for the 60/40, 50/50 PLA/NR blend, both types of clay particles induce toughening effect in different way with the 70/30 PLA/NR blend. As NR content increases from 30 wt% to 50 wt%, the tensile strength and elongation at break decrease due to the increasing relative portion of NR of low tensile modulus within the PLA/NR blend and decreasing interfacial area between PLA and NR as shown in Fig. 2. In the case of the PLA/NR 50/50 blend, the addition of 2 wt% C20A improves the elongation at break to 46% (Fig. 4 (c)). However, it decreases the tensile strength from 6 MPa to less than 1 MPa. The addition of 0.5 and 2 wt% C20A increases bonding between two phases while decreasing the ability of the blend to resist the stress due to the dispersion of particles. For the PLA/NR 50/50 with CNa\(^+\), the increase of elongation at break appears to stem from the additional energy dissipation between the agglomerates of CNa\(^+\) and PLA.

The observations show that there exists an optimal content of clay particles for PLA/NR toughening depending on blend morphology. Further study is essential to find the optimal morphology controlled by clay particles less than 1 wt%.

### 4. CONCLUSIONS

In this study, the toughening effect of clay particles on PLA/NR blend was investigated based on morphological and rheological analysis. PLA was mixed with natural rubber and clay particles by varying the concentration of the NR phase and the type of clay particle (CNa\(^+\), C20A). Depending on the composition of PLA/NR blend, the blend had different morphology from droplet structure to apparent co-continuous structure. Different from the expectation that the blend shows the higher ductile behavior with increasing NR content, the PLA/NR blend with the apparent co-continuous structure decreased mechanical tensile properties with poor bonding between two phases. For those blends, two different clays (CNa\(^+\), C20A) affected the blend morphology in different way due to different localization behavior of clay in the blend as well as the degree of dispersion. In the case of PLA/NR 70/30 blend of droplet structure, only the addition of 0.5 wt% of C20A impressively improved elongation at break of the blend from 50% to 60%. For the droplet morphology, a small amount of clay particles increased interfacial area and induced better bonding between phases. Meanwhile, for the apparent co-continuous blend, tensile performance improved as the clay content increases regardless of the type of clay due to the complex effect of clay to the interface as well as PLA phase.
ACKNOWLEDGEMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2016R1E1A1A01942362).

REFERENCES

1) Nofar M, Maani A, Sojoudi H, Heuzey MC, Carreau PJ, *J Rheol*, 59, 317 (2015).
2) Pluta M, Jeszka JK, Boiteux G, *Eur Polym J*, 43, 2819 (2007).
3) Johnsen BB, Kinloch AJ, Mohammed RD, Taylor AC, Sprenger S, *Polymer*, 48, 530 (2007).
4) Perkins WG., *Polym Eng Sci*, 39, 2445 (1999).
5) Johnsen BB, Taylor AC, *Polymer*, 46, 7352 (2005).
6) Zolali AM, Heshmati V, Favis BD, *Macromolecules*, 50, 264 (2017).
7) Bitinis N, Verdejo R, Cassagnau P, Lopez-Manchado MA, *Mater Chem Phys*, 129, 823 (2011).
8) Swallowe GM, "Mechanical Properties and Testing of Polymers", (1999), Springer, Berlin.
9) Wu S, *Polymer*, 26, 1855 (1985).
10) Wu S, *Polym Eng Sci*, 30, 753 (1990).
11) Bitinis N, Verdejo R, Maya EM, Espuche E, Cassagnau P, Lopez-Manchado MA, *Compos Sci Technol*, 72, 305 (2012).
12) Bitinis N, Sanz A, Nogales A, Verdejo R, Lopez-Manchado MA, Ezquerra TA, *Soft Matter*, 8, 34 (2012).
13) Hong JS, Namkung H, Ahn KH, Lee SJ, Kim C, *Polymer*, 47, 3967 (2006).
14) Hong JS, Kim YK, Ahn KH, Lee SJ, *J App Polym Sci*, 108, 565 (2008).
15) Lee S, Kim M, Song HY, Hyun K, *Macromolecules*, 52, 7904 (2019).
16) Wu S, *Polym Eng Sci*, 27, 335 (1987).
17) Lee S, Lee, JW, *Korea-Aust. Rheol J*, 17, 71 (2005).
18) Ho CC, Khew MC., *Langmuir*, 16, 1407 (2000).
19) Biresaw G, Carriere CJ, *J Polym Sci Part B Polym Phys*, 39, 920 (2001).
20) Elias L, Fenouillot F, Majesté JC, Martin G, Cassagnau P, *J Polym Sci Part B Polym Phys*, 46, 1976 (2008).
21) Ock HG, Kim DH, Ahn KH, Lee SJ, Maia JM, *Eur Polym J*, 76, 216 (2016).
22) Dalai EN, *Langmuir*, 3, 1009 (1987).
23) Baudouin AC, Devaux J, Bailly C, *Polymer*, 51, 1341 (2010).
24) Pötschke P, Pegel S, Claes M, Bonduel D, *Macromol Rapid Commun*, 29, 244 (2008).