

Natural rubber-based mechanical modifiers for poly(lactic acid)

Wasan Tissanan¹ and Pranee Phinyocheep^{1*}

Received November 6, 2020; Revised November 16, 2020; Accepted December 9, 2020

Abstract

Poly(lactic acid) (PLA), a compostable and biodegradable polymer, is a high-brittle polymeric material. Therefore, mechanical property improvement of the PLA is challenging by utilization of natural rubber (NR), a green elastomeric and renewable materials. In this study, NR and chemically modified NR to epoxidized NR (ENR) are explored as impact modifiers for the PLA. The as-prepared ENR with 30 mol% epoxide content (E30NR) and NR are melt-blended with PLA at various rubber contents (1 to 5 wt.%). The result illustrates the concurrent increment in elongation ability and impact performance of PLA, approximately elevenfold and twofold, respectively, with adding 5 wt.% E30NR compared with those of NR/PLA blends with the same rubber content. In addition, the 5 wt.% E30NR is an efficient impact modifier for PLA as the elongation at break and the impact strength is increased approximately fifteen and four times, respectively, compared to the PLA. The E30NR/PLA blends launch superior modulus and strength when compared to NR/PLA blends. Furthermore, E30NR/PLA films transparency demonstrated from transmittance percentage shows higher transparency than NR/PLA blend films. Consequently, NR-based utilization as a mechanical modifier could be considered a sustainable and alternative way for the value-added of NR and increment of PLA's applications.

Keywords: Impact modifier; Natural rubber; Poly(lactic acid); Sustainable development

Introduction

Natural rubber (NR) is a bio-based and renewable material received from the *Hevea brasiliensis* tree, consisting mainly of cis-1,4 isoprene units (Toki et al., 2002). NR has a number of outstanding aspects, for instance, high flexibility and high tensile strength, as well as biodegradability (Smitthipong et al., 2016). Therefore, it has been utilized as a raw material in several products, ranging from personal protective equipment and medical devices to car and aircraft tires (Thomas & Mathew, 2011). The rubber plantations of Thailand are distributed across all regions of the country. It is one of the agricultural products with mass production in Thailand, the world's largest natural rubber producer (Pyay et al., 2019). Over the years, the high rubber production rate has severely unbalanced the demand and supply gap resulting in a dramatic drop in natural rubber prices. In addition, the unsaturated hydrocarbon structure of NR causes some drawback properties such as low heat and

thermal resistance, and low oil resistance. Therefore, modification of NR structure has been widely studied to improve these disadvantages, and widen its area of applications. For instance, hydrogenation and epoxidation are chemical modification techniques to increase the heat resistance and oil resistance of the rubber (Saengdee et al., 2020). Furthermore, the development of NR for the additive in plastic is an emerging and interesting challenge. This concept of NR's utilization is considered for the value-added of rubber and the increasing plastic applications.

Poly(lactic acid) (PLA), a compostable and biodegradable polymer, is obtained from natural feedstocks, such as rice, corn, and wheat with clean-productive manufacturing (Hamad et al., 2015). Nowadays, we are facing plastic waste problem from petroleum-based plastic as it is not compostable and required several years for partial degradation. Therefore, the PLA has been increasingly demanding for various plastic prod-

¹ Department of Chemistry and Rubber Technology Research Centre, Faculty of Science, Mahidol University, Rama VI Road, Payathai, Bangkok 10400 Thailand

*Corresponding author: E-mail: pranee.phim@mahidol.ac.th Tel: 66-0890493028

ucts. However, the PLA is a high-brittle plastic because of high glass transition temperature (T_g) approximately 55-60 °C, limiting its applications (Becker et al., 2010). Blending of an elastomeric material with the PLA is one of the techniques to improve the performance of PLA. NR which is a bio-based and renewable material mentioned earlier, is a good candidate to toughen the PLA. However, the effectiveness of NR for toughening PLA is still insufficient due to the poor interfacial interaction coming from the difference in the polarity between NR and PLA phases (Bitinis et al., 2011). Consequently, several researchers have dedicated to modifying NR-based products to improve the mechanical performance of PLA. Many types of the as-prepared rubbers by the escalating polarity of rubber, such as NR grafted with poly(butyl acrylate) (Zhang et al., 2011), NR grafted with glycidyl methacrylate (Juntuek et al., 2012), hydroxyl epoxidized NR (Phetphaisit et al., 2019), and epoxidized hydrogenated NR (Tessanan et al., 2020), have deliberately been utilized for blending PLA. Nowadays, many attempts to improve PLA's mechanical properties using NR and its derivatives have been paid to increase the value-added NR and widespread applications of PLA. This concept may be regarded as a sustainable way for practical development.

In this work, epoxidized NR was prepared via epoxidation reaction under the latex medium, and it is considered a green process (Tessanan et al., 2020). The idea for attaching epoxide groups is to increase the polarity of rubber. Epoxidized NR containing 30 mol% epoxide content (E30NR) is prepared, and the chemical structure of as-synthesized E30NR is asserted using Fou-

rier-transform infrared spectroscopy (FTIR) and proton Nuclear Magnetic Resonance ($^1\text{H-NMR}$) spectroscopy. Afterward, the E30NR is physically melt-blended with PLA by various rubber contents (i.e., 1, 3, and 5 wt.%) using an internal mixer. Mechanical properties (tensile and impact performances) of polymer blends system are investigated. Moreover, the film transparency of ENR/PLA blends is conducted to ensure the mechanical improvement of PLA. Unmodified NR/PLA blends are also prepared in the same weight ratios to compare their performance with the E30NR/PLA blends system.

Experimental procedure

Materials

PLA (2003D) produced from NatureWorks Co. Ltd., USA with melt flow index (MFI) of 6.0 g/10 min (190 °C/2.16 kg). High ammonia natural rubber (HANR) latex was received from Thai Rubber Latex Co. Ltd., Thailand. Hydrogen peroxide (35%w/w) was supplied by QRec, New Zealand. Formic acid was purchased from Carlo Erba Reagent, USA.

Preparation of epoxidized NR

Epoxidized NR was prepared in the latex stage, a green process, with a condition following Tessanan and co-workers (Tessanan et al., 2020). Briefly, 0.15 mol formic acid and 0.62 mol hydrogen peroxide were simultaneously added into 600 mL NR latex (20%DRC) at 60 °C for 20 h. At the end of reaction, epoxidized NR was received and coagulated by methanol followed by several times of washing by water. The schematic preparation of epoxidized NR is shown in Figure 1.

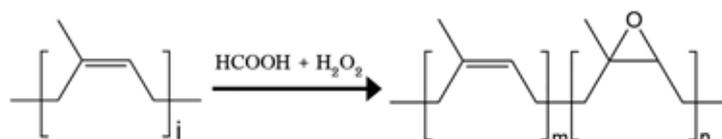


Figure 1. Schematic preparation of epoxidized NR in latex stage

Rubber/PLA blends

PLA and rubbers (NR and E30NR) were dried in a vacuum oven at 50 °C for 48 h to remove humidity. PLA pellets were melt-blended with various amounts of rubber content ranged from 1 to 5 wt.% using an internal mixer (HAAKE™ Rheomix 90). The mixing condition was operated at 170 °C with a 50rpm rotor speed for 15 min. The blend compositions are summarized in Table 1. After the end of mixing, the blends were taken out and cooled to ambient temperature before grinding by a grinder machine. All granulated rubber/PLA blends were dried in a vacuum oven at 40 °C for 48 h and kept in the desiccator.

Characterizations

Chemical structure of NR and E30NR was analyzed by FT-IR analysis (Perkin Elmer-2000). An attenuated total reflectance infrared (ATR-IR) mode was operated in the range of wavenumber between 4000-400 cm^{-1} with 32 scans and a resolution of 4 cm^{-1} . $^1\text{H-NMR}$ analysis (AM 400 spectroscopy 300 MHz) was utilized to assert the chemical structure of modified NR. 10 mg of sample was dissolved in deuterated chloroform (CDCl_3) for measurement. The percentage of epoxidation of E30NR was calculated from the integrated peak areas from $^1\text{H-NMR}$ spectrum following equation (1).

$$\% \text{ Epoxidation content} = \left[\frac{A_{2.70}}{A_{2.70} + A_{5.10}} \right] \times 100 \quad (1)$$

$A_{2.70}$ and $A_{5.10}$ are the integrated peak areas of methine protons adjacent to the epoxide and methine protons of the double bond units.

Thermal decomposition of rubber was measured by a thermal gravimetric analyzer (Mettler, Q500/TA Instrument). Approximately 10 mg of rubber was performed with heating from 40 °C to 600 °C using a heating rate of 10 °C/min under nitrogen atmosphere.

Thermal transition relaxation of samples was investigated by using a differential scanning calorimeter (Perkin Elmer DSC 7). Rubbers were carried out from 40 °C to 600 °C by a heat-cool-heat cycle with a heating rate of 10 °C/min.

Uniaxial tensile behavior of PLA blends was operated following ASTM D882 using a universal testing machine (Instron 5566). Twelve rectangular sheets with dimensions 10x90x0.5 mm^3 were measured at 50 mm/min crosshead speed with static load cell of 1 kN under room temperature (25 ± 2 °C).

Impact performance was carried out following ASTM D256 by impact tester (Zwick 5102 Pendulum). Six specimens were notched and operated under the Izod mode test at room temperature (25 ± 2 °C).

Transparency of PLA blend films was determined by a UV-Vis spectrophotometer (JASCO V-530, Perkin Elmer) with the 400 to 700 nm scanning wavelength. The 100- μm film thickness was prepared by compression molding at 170 °C for 2 min under the 105 bars pressure.

Table 1. Rubber/PLA blend compositions.

Samples	PLA (wt.%)	NR (wt.%)	E30NR (wt.%)
Neat PLA	100	-	-
NR/PLA (1/99)	99	1	-
NR/PLA (3/97)	97	3	-
NR/PLA (5/95)	95	5	-
E30NR/PLA (1/99)	99	-	1
E30NR/PLA (3/97)	97	-	3
E30NR/PLA (5/95)	95	-	5

Results and discussion

Chemical structure and thermal properties of epoxidized NR

FTIR spectra of NR and E30NR are illustrated in Figure 2. NR spectrum demonstrates the specific absorption peaks at 1664 and 836 cm^{-1} , belonging to C=C stretching and C=C-H out-of-plane bending vibrations, respectively (Fig. 2a). After the epoxidation reaction, the epoxidized NR spectrum still shows NR's characteristic peaks, and, moreover, it provides the new peaks at 1245 and 875 cm^{-1} , attributing to symmetric and asymmetric C-O-C stretching vibrations, respectively. Moreover, there is a slight decline in the intensity variation of carbon-carbon-double bond peaks observed at 1664 cm^{-1} , compared to the absorption peak at 1375 cm^{-1} (CH₃ bending vibration) of the epoxidized NR spectrum. It can

illustrate the change in unsaturation units into epoxide units of rubber after epoxidation reaction. Figure 3 shows ¹H-NMR spectra of NR and E30NR. As a result, NR reveals the unique signals at 5.10 ppm (a), 2.03 ppm (a'), and 1.67 ppm (a''), belonging to methine protons nearby isoprene unit, methylene protons, and methyl protons, respectively. Meanwhile, epoxidized NR still shows the characteristic signal of the virgin NR and observed the two-new peaks at 1.30 ppm (c), and 2.70 ppm (d), assigning to methyl protons and methine protons of the epoxide ring, respectively (Phinyocheep et al., 2005; Samran et al., 2005). In addition, as calculated epoxide content following equation (1), the epoxidized NR consists of 29.63 mol% epoxide content and is defined as E30NR.

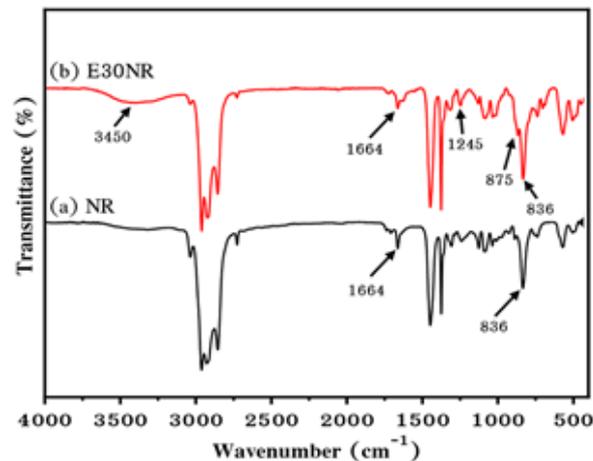


Figure 2. FT-IR spectra of (a) NR and (b) E30NR.

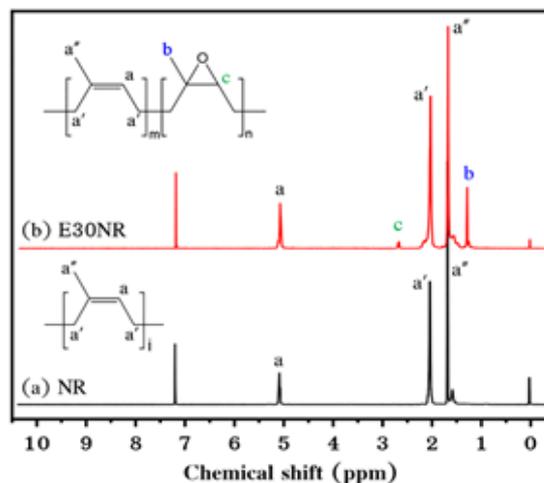


Figure 3. ¹H-NMR spectra of (a) NR and (b) E30NR.

Thermal resistance of rubbers was evaluated by TGA analysis, as presented in Figure 4. The decomposition temperature, including onset decomposition temperature (T_o), fastest decomposition temperature (T_f), and final decomposition temperature (T_n) of rubbers, were measured. The results show that NR begins to decompose at approximately 290 °C and undergoes the fastest decomposition rate at about 348 °C before it completes at approximately 425 °C. The thermal resistance of E30NR is demonstrated at approximately 312 °C (T_o), 364 °C (T_f), and 442 °C (T_n). The attaching epoxide groups along the NR backbone provides higher thermal-resistant material. This result may be due to the characteristic nature of epoxide-based material, having high chemical and thermal resistance (Sun et al., 2018).

Furthermore, the thermal relaxation behavior of rubbers (NR and E30NR) was conducted using DSC analysis, as shown in Figure 5. The T_g of NR appeared at approximately -65 °C. After the epoxidation reaction, the T_g of NR shifts from -65 °C towards the high-temperature zone at -34 °C (E30NR). This phenomenon can be described to the attaching rigid-epoxide ring onto NR molecular chains, resulting in the restriction of the segmental-chain motion (Hamzah et al., 2016).

Mechanical properties

Tensile properties (Young's modulus, Tensile strength, elongation at break) of rubber/PLA blends system are demonstrated in Figure 6-8. Young's modulus and tensile strength of neat PLA are 2.00 GPa and 62.4 MPa, respectively, with only 6.18% elongation at

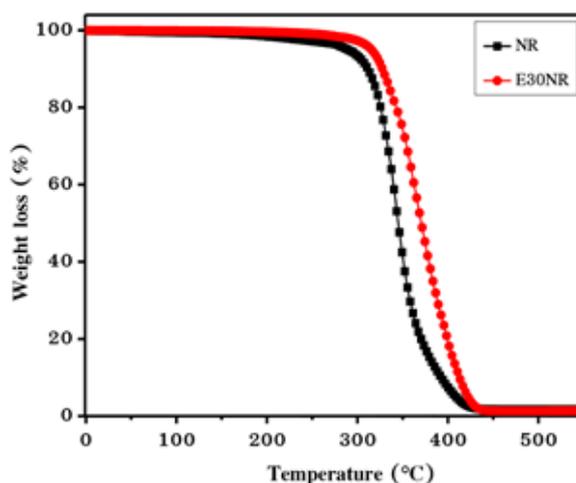


Figure 4. Thermal decomposition of (a) NR and (b) E30NR.

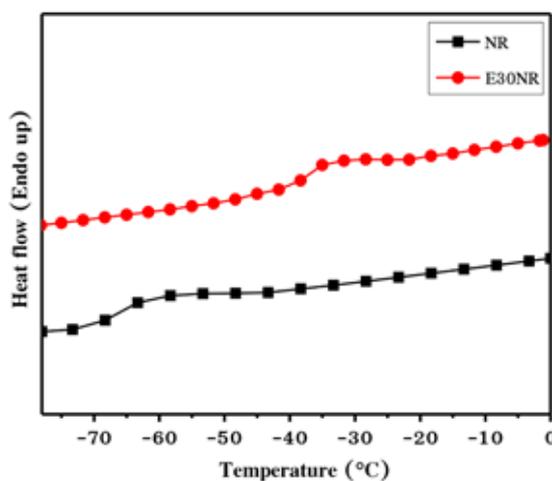


Figure 5. DSC thermograms of (a) NR and (b) E30NR.

break. The addition of rubber reduces the modulus of PLA in the blends with increasing rubber contents. The moduli values tend to reduce from 2.00 GPa (neat PLA) into 1.61 GPa (NR/PLA blend) and 1.75 GPa (E30NR/PLA blend) containing 5 wt.% rubber (Figure 6). The E30NR/PLA blends at different rubber content have higher moduli than the NR/PLA blends at the same rubber content. Figure 7 illustrates the gradual reduction of the uniaxial tensile strength by adding rubber contents. The strength values decline from 62.4 MPa (neat PLA) down to 34.65 MPa (NR/PLA blend) and 40.60 MPa (E30NR/PLA blend), consisting of 5 wt.% rubber. The E30NR/PLA blends provide higher values of strength compared to that of NR/PLA blends, followed by PLA. This result could be explained due to the addition of elastomeric material into the hard-brittle polymer, leading to the

decrement in stiffness and strength (Bitinis et al., 2011; Zhang et al., 2011). The improving polarity of rubber in E30NR can escalate the interfacial interaction between rubber and PLA phases, resulting in the improving modulus and strength compared to NR/PLA blends (Rosli et al., 2016). Considered on elongation ability as displayed in Figure 8, NR/PLA blends increase slightly from 6.18% (neat PLA) to 8.49% (5 wt.% NR). Meanwhile, E30NR/PLA blends upsurge to 89.38% (5 wt.% E30NR). At 5 wt.% rubber content, the elongation ability of E30NR/PLA blend is elevenfold and fifteenfold when compared to NR/PLA blend and neat PLA, respectively. As a result, it can attribute that the improving polarity of NR with epoxide groups could enhance the compatibility between rubber and PLA matrix.

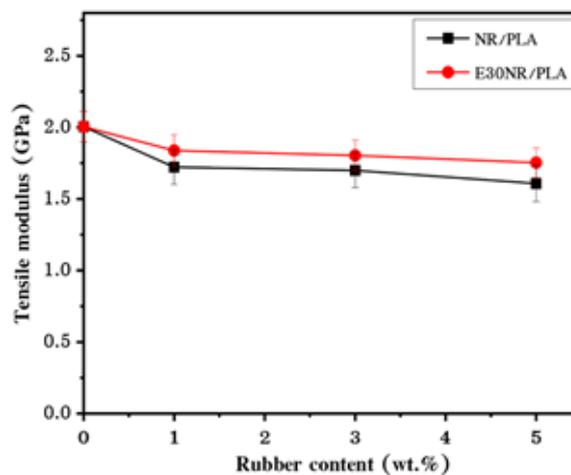


Figure 6. Tensile modulus of rubber/PLA blends at various rubber contents (0 to 5 wt.%).

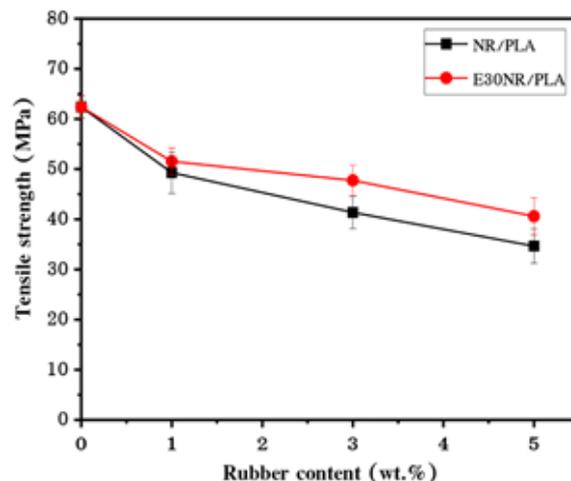


Figure 7. Tensile strength of rubber/PLA blends at various rubber contents (0 to 5 wt.%).

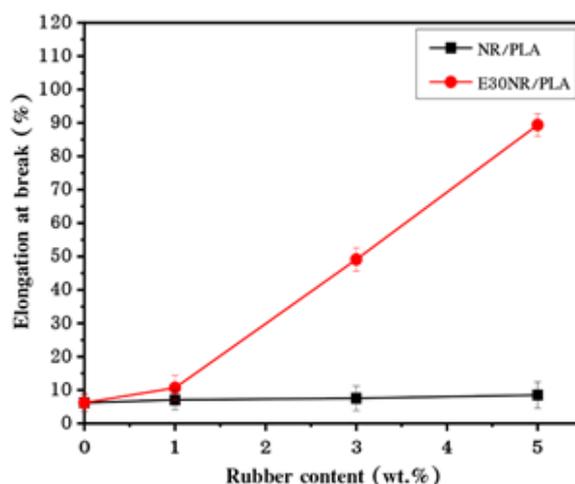


Figure 8. Elongation at break of rubber/PLA blends at various rubber contents (0 to 5 wt.%).

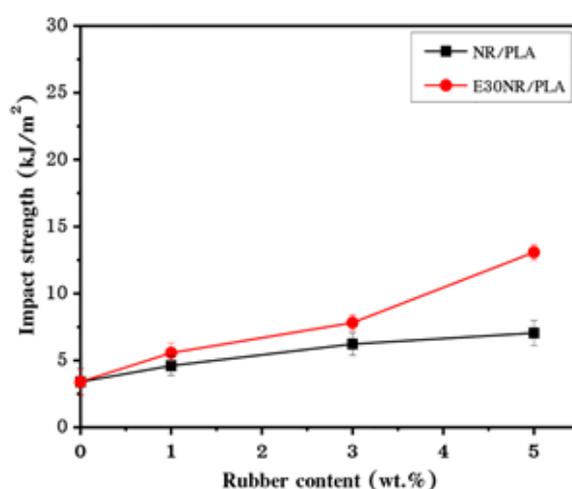


Figure 9. Impact properties of rubber/PLA blends at various rubber contents (0 to 5 wt.%).

The brittleness of the plastic is normally considered by the impact property. The PLA has low impact strength which limit its application. The addition of a soft material should improve its impact strength. Figure 9 shows the impact strength of the rubber/PLA blends system. The addition of rubbers (NR and E30NR) can escalate the toughness of PLA because the elastomeric nature of rubber can act as a stress concentrator for dissipating energy obtained from an external force (Bitinis et al., 2011; Rosli et al., 2016). NR/PLA blends with NR contents (1 to 5 wt.%) reveal the slight increment in the impact strength from 3.40 kJ/m² (neat PLA) towards 7.05 kJ/m² (5 wt.% NR content). In terms of E30NR/PLA blends, the impact strength values boost to the maximum value at 13.08 kJ/m² by adding E30NR contents up to 5 wt.%. The impact performance of E30NR/

PLA (5/95) increases about twofold compared to NR/PLA (5/95) blends and fourfold compared to the neat PLA. This significant enhancement can ascribe to a decrement in interfacial tension and an increment of segmental interaction between the modified rubber and the PLA matrix (Tessanan et al., 2020).

Optical properties

Transparency of plastic sheet is defined as the transmission of visible light in the short range of 540-560 nm, according to ASTM-D1746-03 (Mathlouthi, 1994). The 550-nm wavelength had been chosen to investigate the transmittance percentage of neat PLA and rubber/PLA blend films, as presented in Figure 10. The light transmittance of neat PLA was found at 91.30%, typically high transparent material. The light transmittance of films is reduced with the addition of rubbers (1

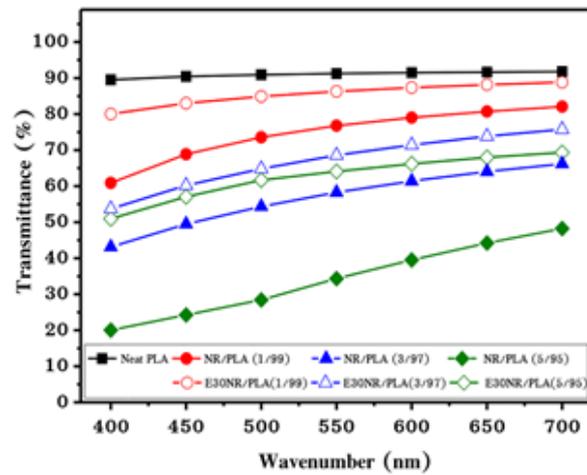


Figure 10. Transmittance percentage of rubber/PLA blend films at various rubber contents (0 to 5 wt.%)

to 5 wt.%). NR/PLA blend films provide light transmittance ranging between 34.34% (5 wt.% NR) to 76.79% (1 wt.% NR). Meanwhile, E30NR/PLA blend films reveal between 64.08% (5 wt.% E30NR) to 86.30% (1 wt.% E30NR). It could be explained that the incompatibility of NR and PLA results in the film's heterogeneity, leading to a decrement of the light transmittance. However, the enhancing polarity of NR to E30NR can escalate the partial compatibility between rubber and PLA, resulting in improved film transparency.

Conclusions

The enhancing potential and effectiveness of NR and modified NR, as mechanical modifiers, for the brittle PLA is still an interesting challenge. In this work, the NR and as-synthesized E30NR were utilized for improving the mechanical properties of PLA. The result reveals the dramatic enhancement in elongation ability and impact performance with the addition of E30NR when compared to NR. The NR could increase slightly

the mechanical properties of the PLA while the E30NR is an efficient impact modifier for PLA. In particular, the 5 wt.% E30NR/PLA could enhance the elongation at break and the impact strength, approximately fifteen and four times, respectively, compared to the neat PLA. Furthermore, the film transparency is improved for E30NR/PLA blends compared to NR/PLA blends. This development was performed to reach the way for high value-added and new potential application of NR as well as PLA, supporting the sustainability concept for saving the Earth.

Acknowledgements

The authors would like to thank partial support of IRPC Public Company Limited for this study. We are thankful to Rubber Technology Research Centre, Faculty of Science, Mahidol University for equipment and facilities. The scholarship of Science Achievement Scholarship of Thailand (SAST) to W.Tessanan is very much appreciated.

References

- Becker, J.M., Pounder, R.J. & Dove, A.P. (2010). Synthesis of poly(lactide)s with modified thermal and mechanical properties. *Macromolecular Rapid Communications* 31, 1923-1937.
- Bitinis, N., Verdejo, R., Cassagnau, P. & Lopez-Manchado, M.A. (2011). Structure and properties of polylactide/natural rubber blends. *Materials Chemistry and Physics* 129, 823-831.
- Hamad, K., Kaseem, M., Yang, H.W., Deri, F. & Ko, Y.G. (2015). Properties and medical applications of polylactic acid: A review. *EXPRESS Polymer Letters* 9, 435-455.
- Hamzah, R., Bakar, M.A., Dahham, O.S., Zulkepli, N.N. & Dahham, S.S. (2016). A structural study of epoxidized natural rubber (ENR-50) ring opening under mild acidic condition. *Journal of Applied Polymer Science* 133, 44123.
- Juntuek, P., Ruksakulpiwat, C., Chumsamrong, P. & Ruksakulpiwat, Y. (2012). Effect of glycidyl methacrylate-grafted natural rubber on physical properties of polylactic acid and natural rubber blends. *Journal of Applied Polymer Science* 125, 745-754.
- Mathlouthi, M. (1994). *Food Packaging and Preservation*. Elsevier Applied Science, Blackie, Glasgow, UK.
- Phetphaisit, C.W., Wapanyakul, W. & Phinyocheep, P. (2019). Effect of modified rubber powder on the morphology and thermal and mechanical properties of blown poly(lactic acid)-hydroxyl epoxidized natural rubber films for flexible film packaging. *Journal of Applied Polymer Science* 136, 47503.
- Phinyocheep, P., Phetphaisit, C.W., Derouet, D., Campistrion, I. & Brosse, J.C. (2005). Chemical degradation of epoxidized natural rubber using periodic acid: Preparation of epoxidized liquid natural rubber. *Journal of Applied Polymer Science* 95, 6-15.
- Pyay, S., Thanungkano, W., Mungkalasiri, J. & Musikavong, C. (2019). A life cycle assessment of intermediate rubber products in Thailand from the product environmental footprint perspective. *Journal of Cleaner Production* 237, 117632.
- Rosli, N.A., Ahmad, I., Anuar, F.H. & Abdullah, I. (2016). Mechanical and thermal properties of natural rubber-modified poly(lactic acid) compatibilized with telechelic liquid natural rubber. *Polymer Testing* 54, 196-202.
- Saengdee, L., Phinyocheep, P. & Daniel, P. (2020). Chemical modification of natural rubber in latex stage for improved thermal, oil, ozone and mechanical properties. *Journal of Polymer Research* 27, 275.
- Samran, J., Phinyocheep, P., Daniel, P. & Kittipoom, S. (2005). Hydrogenation of unsaturated rubbers using diimide as a reducing agent. *Journal of Applied Polymer Science* 95, 16-27.
- Smitthipong, W., Suethao, S., Shah, D. & Vollrath, F. (2016). Interesting green elastomeric composites: Silk textile reinforced natural rubber. *Polymer Testing* 55, 17-24.
- Sun, Z., Xiao, J., Tao, L., Wei, Y., Wang, S., et al. (2018). Preparation of high-performance carbon fiber-reinforced epoxy composites by compression resin transfer molding. *Materials* 12, 13.
- Tessanan, W., Chanthateyanonth, R., Yamaguchi, M. & Phinyocheep, P. (2020). Improvement of mechanical and impact performance of poly(lactic acid) by renewable modified natural rubber. *Journal of Cleaner Production* 276, 123800.
- Thomas Kurian & Mathew, N.M. (2011). Natural Rubber: Production, Properties and Applications, in: Susheel Kalia & Avérous, L. (Eds.), *Biopolymers*. pp. 403-436.
- Toki, S., Sics, I., Ran, S., Liu, L., Hsiao, B.S., et al. (2002). New Insights into Structural Development in Natural Rubber during Uniaxial Deformation by In Situ Synchrotron X-ray Diffraction. *Macromolecules* 35, 6578-6584.
- Zhang, C., Man, C., Pan, Y., Wang, W., Jiang, L., et al. (2011). Toughening of polylactide with natural rubber grafted with poly(butyl acrylate). *Polymer International* 60, 1548-1555.