Formosa Journal of Sustainable Research (FJSR)
Vol.3, No.2, 2024: 273-282

The Influence of Nano Bentonite Filler Material and Cyclic Natural Rubber Grafted Oleic Acid as a Compatibilizer on the Blend of Cyclic Natural Rubber/Polyamide

Barita Aritonang[1*], Ahmad Hafizullah Ritonga[2], Karnirius Harefa[3]
Institut Kesehatan Medistra Lubuk Pakam
Corresponding Author: Barita Aritonang baritaaritonang11@gmail.com

---

ARTICLEINFO

Keywords: Cyclic Natural Rubber, Polyamide, Bentonite, Oleic Acid, Grafting

Received : 1 December
Revised : 18 January
Accepted: 23 February

ABSTRACT

Cyclic natural rubber (CNR) and polyamide (PA) cannot blend homogeneously due to their differing polarities. CNR is nonpolar with low surface tension, while PA is polar with high surface tension. To achieve a homogeneous and compatible CNR/PA blend, a CNR-g-OA compatibilizer is required. This study aims to investigate the influence of CNR-g-OA and nano bentonite on the physical and chemical properties of the PA/CNR mixture. The research findings indicate successful grafting of OA onto CNR, resulting in CNR-g-OA formation. Based on electron microscope structural analysis, the CNR/PA mixture yields a homogeneous and compatible blend. In conclusion, CNR-g-OA and nano bentonite can enhance the quality of the PA/CNR blend by producing a homogeneous and compatible mixture

---

DOI: https://doi.org/10.55927/fjsr.v3i2.8134
ISSN-E: 2830-6228
https://journal.formosapublisher.org/index.php/fjsr

INTRODUCTION

Polyamide (PA) and cyclic natural rubber (CNR) are two distinct types of polymer materials with differing properties and characteristics. CNR is nonpolar, while PA is polar, making them incompatible for achieving homogeneous mixing. The primary reasons behind the incapacity of the PA/CNR blend to mix uniformly and compatibly stem from disparities in polarity and weak surface tension. CNR, a chemically modified derivative of natural rubber achieved through cyclization reactions, offers attributes like low surface tension, rigidity, resistance to abrasion, and exceptional adhesive properties, making it prevalent as a binding agent in paints and printing inks. Conversely, PA, a form of plastic, boasts excellent mechanical characteristics, including tensile strength, elastic modulus, abrasion resistance, and high surface tension, widely utilized in automotive, electronics, and packaging sectors. However, when combined, these two materials tend to exhibit phase separation, hindering homogeneous mixing and compatibility, resulting in poor mechanical properties(Barita Aritonang & Wirjosentono, 2020)(Ritonga et al., 2022)(Chow & Ishak, 2015).

To improve the compatibility of the PA/CNR blend for a uniform and harmonious mixture, the surface of CNR is altered using the oleic acid (OA) monomer and dicumyl peroxide (DCP) initiator through copolymer grafting within an internal mixer during a melt blending process. This method allows the functionalization of CNR based on the covalently bound OA monomer properties without altering the fundamental CNR structure. The choice of the grafting technique within an internal mixer is due to its simplicity, cost-effectiveness, and minimal environmental impact. OA and DCP serve as compatibilizers to enhance the compatibility of the PA/CNR blend. Oleic acid establishes hydrogen bonds with water, reducing interfacial tension within the blend, while Dicumyl peroxide reacts with CNR, forming cross-links to enhance the strength and elastic modulus of the composite material. Additionally, natural resource-based filler materials like bentonite, containing montmorillonite, are used to enhance interfacial homogeneity due to their plate-like morphology, inert properties, non-flammability, and extensive specific surface area. The addition of nano-scale filler materials aims to address degradation resistance and enhance mechanical properties(B. Aritonang et al., 2020)(Ritonga et al., 2023).

Previous research successfully modified CNR with various monomers through copolymer grafting techniques. For instance, Barita Aritonang et al. reported the grafting process of OA onto the CNR molecular chain, resulting in CNR-g-OA. Similarly, research by B. Aritonang et al. reported the successful grafting process of CNR with the OA monomer using dicumyl peroxide, resulting in CNR-g-OA(Bandyopadhyay & Ray, 2018)(Sapsrithong et al., 2020).

Based on this background, this study aims to analyze the effect of CNR-g-OA compatibilizer and nano bentonite on the physical and chemical properties of PA/CNR blends through copolymer grafting in an internal mixer.

LITERATURE REVIEW

Polyamide (PA) and cyclic natural rubber (CNR) are two types of polymer materials with different polarity properties. CNR exhibits nonpolar characteristics with low surface tension, while PA is polar with high surface tension. This difference leads to an inability to achieve homogeneous mixing between them. The main challenge in mixing PA and CNR is the mismatch in polarity and weak intermolecular forces, resulting in an uneven mixture and inferior mechanical properties. To address this issue, the use of compatibilizers has been proposed to enhance the intermolecular interactions between the two materials. Additionally, modifying the CNR surface is also considered an approach to improve compatibility with PA. Although there are still challenges in achieving homogeneous mixing between PA and CNR, research efforts continue to develop more effective methods. Homogeneous and compatible mixing between PA and CNR is expected to enhance their application prospects in various industries(Barita Aritonang & Wirjosentono, 2020)(Ritonga et al., 2022)(Chow & Ishak, 2015).

Hypothesis

The CNR-g-OA compatibilizer and nano bentonite can enhance the surface tension properties of CNR/PA, resulting in a homogeneous and compatible mixture.

METHODOLOGY

The equipment used in this research includes an analytical balance, beakers, a magnetic stirrer, a hot plate, a separating funnel, pipettes, viscosity measurement instruments, an internal mixer, a Fourier transform infrared (FT-IR) spectrophotometer, a Scanning Electron Microscope (SEM). The materials used in this study include cyclic natural rubber (Resiprena-35) produced by Resiprena Factory, PT. Industri Karet Nusantara, Sei Bamban, Tebing Tinggi, North Sumatra, polyamide, oleic acid p.a, dicumyl peroxide p.a, toluene p.a, N-heptane p.a, acetone p.a, xylene p.a

The Grafting Process of OA into the CNR Molecular Chain Using Dicumyl Peroxide Initiator.

A total of 70 grams of CNR were gradually introduced into the chamber of the internal mixer at a temperature of 160°C and left for approximately 4 minutes until completely melted. Subsequently, 30 phr of OA and 0.5 phr of DCP initiator were added together until the mixture became homogeneous. The mixing process was carried out for 8 minutes at a speed of 80 rpm, and the process was terminated after the CNR-g-OA grafting process occurred. Characterization was performed using FT-IR and SEM.

Table 1. Formulation of OA Grafting Onto the CNR Molecular Chain with and without the Use of DCP Initiator

Sample Code	**CNR (phr)**	**OA (phr)**	**DCP (phr)**
CNR-g-OA	70	30	-
CNR-g-OA	70	30	0.5

(Phr = Parts Hundred Rubber)

1. Blending PA/CNR without the use of CNR-g-OA Compatibilizer and Nanobentonite

The blending process of PA/CNR was conducted within the Thermo Haake Polydrive internal mixer. The concentration of the PA/CNR blend formulation can be seen in Table 2. A total of 20 grams of CNR was introduced into the internal mixer chamber at a temperature of 160°C for 4 minutes with a rotor speed of 60 rpm. After the CNR had melted, 80 grams of PA were added to the internal mixer chamber. The blending process of PA and CNR was carried out for 8 minutes until a homogeneous and compatible mixture was obtained, followed by characterization with FT-IR and SEM.

Table 2. PA/CNR Blend Without CNR-g-OA Compatibilizer

Sample Code	PA (% b/b)	CNR (% b/b)
PA/CNR	80	20
	70	30

2. The PA/CNR Blend Using CNR-g-OA Compatibilizer

The composition of the PA/CNR/CNR-g-OA compatibility blend can be seen in Table 3. The compatibilizer used in the PA/CNR blend is CNR-g-OA. A total of 20 grams of CNR were introduced into the internal mixer chamber at a temperature of 160°C with a rotor speed of 60 rpm for 4 minutes. After the CNR had melted, 80 grams of PA were added to the chamber and processed for 4 minutes. Then, 1% of the CNR-g-OA compatibilizer was added, and the process continued for 4 more minutes. The composition of the PA/CNR/CNR-g-OAblend can be found in Table 3.

Table 3. PA/CNR Blend with CNR-g-OACompatibilizer

Sample Code	**PA (% b/b)**	**CNR (% b/b)**	**CNR-g-OA (% b/b)**	**Nano bentonite (% b/b)**
PA/CNR	80	20	2	-
	80	20	2	1
	80	20	2	2

RESEARCH RESULTS

Analysis of CNR-g-OA FT-IR spectrum

To confirm the success of the copolymer grafting process of OA onto the CNR molecular chain before and after the addition of the DCP initiator, it can be observed through the FT-IR spectrum analysis.

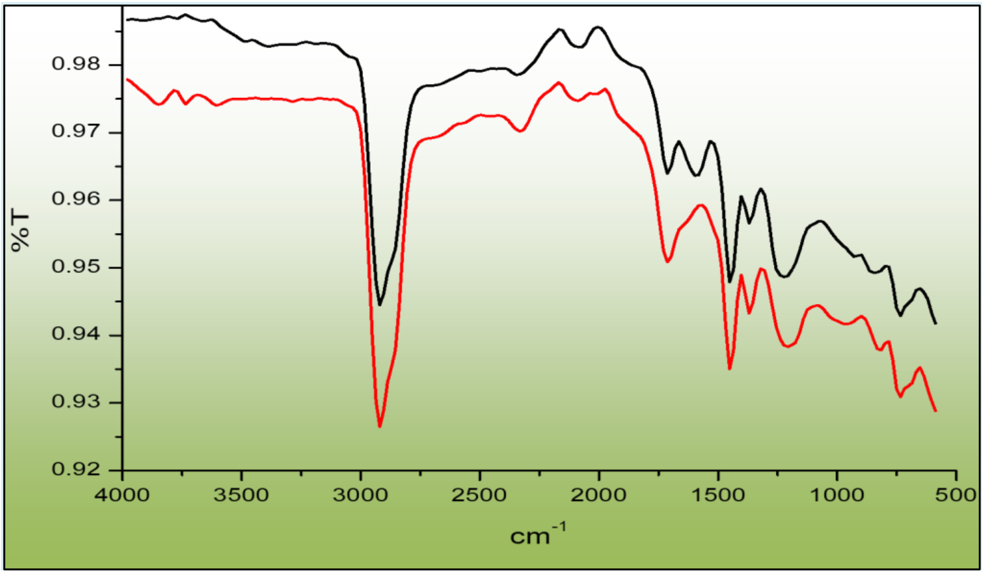

Figure 1. Analysis of CNR-g-OA FT-IR Spectrum

SEM analysis of the morphological structure of the nanocomposite blend of PA and CNR using a CNR-g-OA compatibilizer

The PA/CNR blend is incompatible and does not mix homogeneously, tending to form phase separation. This is due to the differences in polarity and surface adhesion properties between PA and CNR. These differences make it challenging for CNR to distribute within the PA matrix, resulting in a weak interface. To determine whether the PA and CNR mixture is incompatible and homogeneous, one can refer to the surface morphology observed with SEM, as shown in Figures 2 and 3.

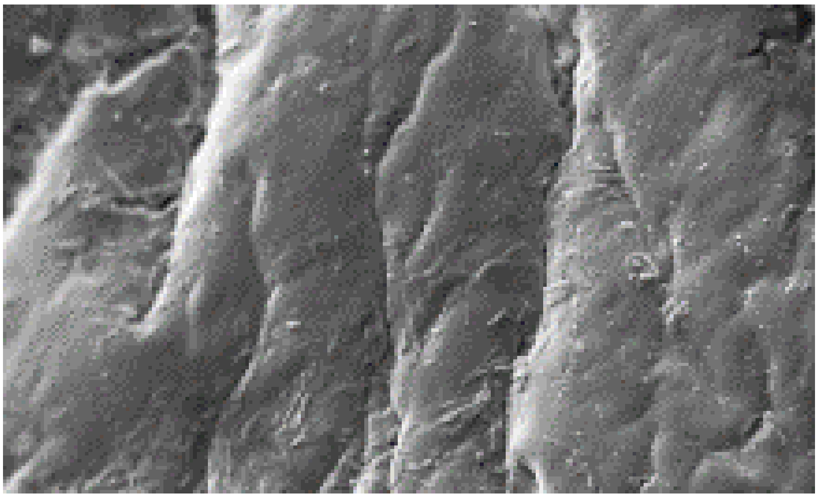

Figure 2. SEM Surface Morphology of PA/CNR Blends without CNR-g-OA Compatibilizer

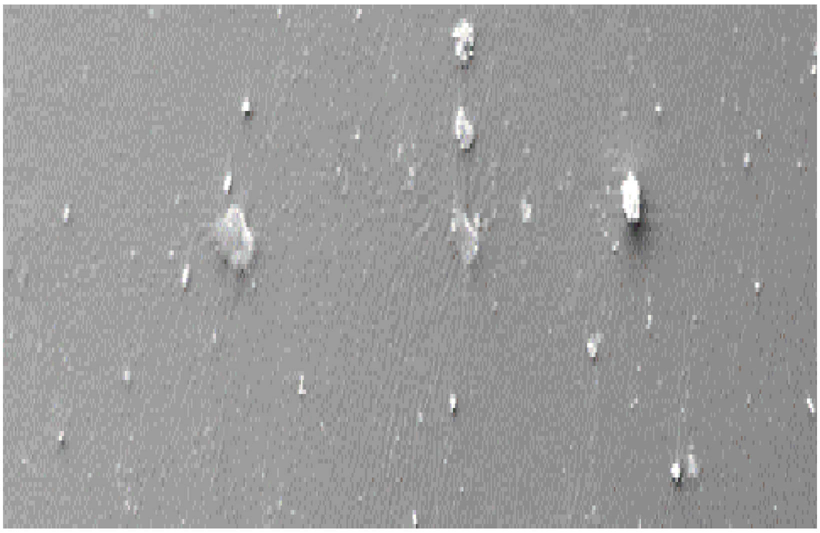

Figure 3. SEM Surface Morphology of PA/CNR Blend Using CNR-g-OA Compatibilizer

SEM analysis of the morphological structure of the nanocomposite blend of PA and CNR using CNR-g-OA compatibilizer and nano bentonite filler.

Nano bentonite will be utilized in this study as a filler to enhance the compatibility of the PA and CNR alloy. To observe the morphological structure of the PA/CNR nanocomposite before and after the addition of nano bentonite filler, please refer to Figures 4 and 5.

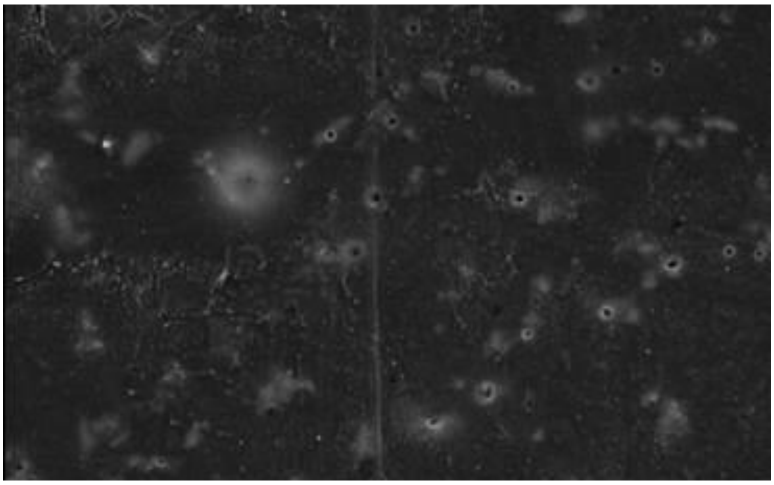

Figure 4. Morphological Structure of the Nanocomposite Blend of PA and CNR Using 2% CNR-g-OA Compatibilizer and 1% Nano Bentonite Filler

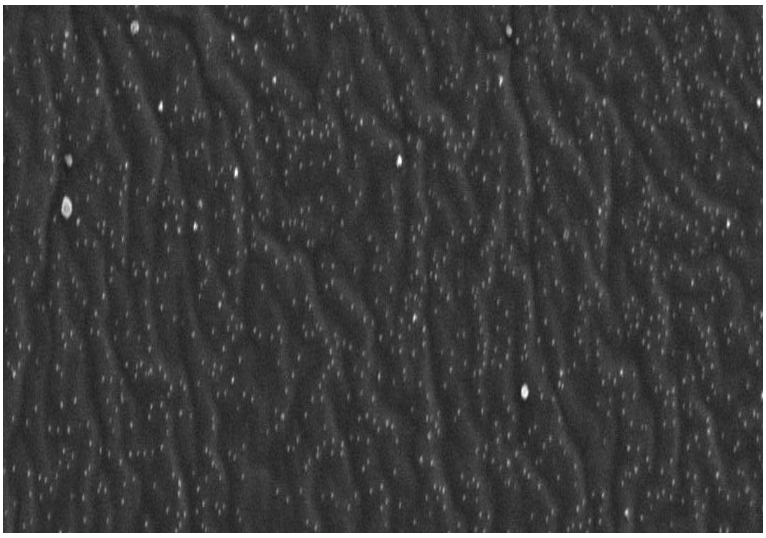

Figure 5. Morphological Structure of the Nanocomposite Blend of PA and CNR Using 2% CNR-g-OA Compatibilizer and 2% Nano Bentonite Filler

DISCUSSION

Based on Figure 1, the spectral region at a wavenumber of 2924.09 cm^{-1} indicates the presence of C-H stretching from the methyl CH_3 functional group originating from CNR. The absorption peak at a wavenumber of 1715 cm^{-1} indicates the presence of the carboxylate carbonyl group C=O derived from oleic acid that has been grafted onto the CNR molecular chain, further supported by the absorption peak at a wavenumber of 1122 cm^{-1}, indicating the presence of C-O stretching from DCP. This confirms that OA has been successfully grafted onto the CNR molecular chain, resulting in the product(Narayanan et al., 2021).

Figure 2 displays the morphology of the PA/CNR blend prepared without a compatibilizer. As a result, the mixture appears to be non-homogeneous and incompatible. It can be observed that the blend tends to separate into two phases that do not integrate. This is due to the agglomeration of CNR with the polyamide matrix, resulting in a morphology characterized by clustered and stacked structures. This is evident from the presence of coarse, large hollow particles that are not evenly and homogeneously dispersed within the PA matrix. The primary reason for this is the poor surface adhesion between the two polymer materials. Research conducted by(Banerjee et al., 2018) supports this statement. They reported that the PA and CNR blend cannot mix (immiscible) due to differences in polarity and very weak surface adhesion properties.

Figure 3 depicts the homogeneous and compatible morphological structure of the PA/CNR blend, which has been enhanced by the addition of a 1% CNR-g-OA compatibilizer. This structure demonstrates a significant improvement compared to the structure without CNR-g-OA compatibilizer, as shown in Figure 2. It can be observed that the resulting mixture has small-sized particles that are evenly and homogeneously dispersed. Although there are still some voids, this is attributed to the relatively minimal amount of compatibilizer added to the PA and CNR blend. However, even in small quantities, this compatibilizer is capable of bridging the previously immiscible polymer mixture of polar and nonpolar polymers, turning it into a miscible polymer blend. This allows certain parts of the CNR structure to interact physically with the surface of the PA. Research by(Chow et al., 2003) and (Liang & Williams, 1992) supports these findings, reporting that the addition of PP-g-MA compatibilizer to Nylon/Polypylene blends in very small amounts can yield a homogeneous and compatible mixture. This addition of a compatibilizer also enhances surface adhesion properties, resulting in a more homogeneous and compatible blend compared to blends without the compatibilizer.

Figure 4 depicts the morphological structure of the nanocomposite blend of PA and CNR using 2% CNR-g-OA compatibilizer and 1% nanobentonite filler. It shows a homogeneous and compatible morphological structure overall, with the nanobentonite filler evenly and homogeneously distributed throughout the PA and CNR alloy. Although there are still some small empty voids present, the addition of compatibilizer and filler in nanoparticle scale has proven to enhance the adhesion properties between the surfaces of the composite materials, resulting in a homogeneous and compatible mixture(Karaağaç & Deniz, 2013).

Figure 5 illustrates the morphological structure of the nanocomposite blend of PA and CNR using 2% CNR-g-OA compatibilizer and 2% nano bentonite filler. It shows a more homogeneous and compatible morphological structure compared to the addition of 1% nano bentonite filler (Figure 4). All the nano bentonite fillers are evenly and homogeneously distributed within the PA and CNR blend, with no more empty voids observed. This is attributed to the significant amount of filler added to the PA and CNR alloy, which enhances the compatibility of the nanocomposite. The more compatibilizer and filler added to the PA and CNR blend, the higher the surface adhesion properties, resulting in a compatible and homogeneous surface morphology of the mixture(Karaağaç & Deniz, 2013).

CONCLUSION AND RECOMMENDATIONS

The addition of 2% CNR-g-OA compatibilizer into the PA and CNR blend enhances the compatibility of the PA/CNR alloy, resulting in a homogeneous and compatible mixture. This is evidenced by SEM morphological structure analysis, showing chemical interactions between PA and CNR. All CNR-g-OA particles are uniformly and homogeneously dispersed within the PA matrix, producing a homogeneous and compatible mixture, thereby eliminating any empty voids on the surface of the PA/CNR alloy. The addition of 2% CNR-g-OA compatibilizer and 2% nanobentonite filler respectively into the PA and CNR blend improves the interface homogeneity of the PA/CNR alloy, resulting in a homogeneous and compatible mixture. This is supported by SEM morphological structure analysis, where no empty voids are observed on the surface of the PA/CNR nanocomposite. All nanobentonite filler materials are evenly dispersed within the PA and CNR blend, yielding a homogeneous and compatible mixture.

FURTHER RESEARCH

This research has limitations regarding the solvents used; to dissolve CNR, xylene is required, while for polyamide, HCL and acetone are necessary. All three solvents are relatively expensive.

THANK YOU

We would like to express our sincere gratitude to the Medistra Lubuk Pakam Health Institute for their support, which enabled us to successfully complete this research.

REFERENCES

Aritonang, B., Tamrin, Wirjosentono, B., & Eddiyanto. (2020). Grafting copolymer cylic natural rubber with oleic acid using dicumyl peroxide as initiator. *AIP Conference Proceedings, 2267.* https://doi.org/10.1063/5.0025153

Aritonang, Barita, & Wirjosentono, B. (2020). Effect of Graft copolymerization of oleic acid on to cyclic natural rubber in polyamide. *Case Studies in Thermal Engineering*, *21*, 100690.

Bandyopadhyay, J., & Ray, S. S. (2018). Structural Characterization of Polymer Nanocomposites. In *Processing of Polymer-based Nanocomposites* (pp. 87–126). Springer.

Banerjee, S. S., Janke, A., Gohs, U., & Heinrich, G. (2018). Electron-induced reactive processing of polyamide 6/polypropylene blends: Morphology and properties. *European Polymer Journal*, *98*, 295–301.

Chow, W. S., & Ishak, Z. A. (2015). Polyamide blend-based nanocomposites: A review. *Express Polymer Letters*, *9*(3).

Chow, W. S., Ishak, Z. A. M., Karger-Kocsis, J., Apostolov, A. A., & Ishiaku, U. S. (2003). Compatibilizing effect of maleated polypropylene on the mechanical properties and morphology of injection molded polyamide 6/polypropylene/organoclay nanocomposites. *Polymer*, *44*(24), 7427–7440.

Karaağaç, B., & Deniz, V. (2013). Interphase Modification and Compatibilization of Rubber Based Blends. In *Advances in Elastomers I* (pp. 263–281). Springer.

Liang, Z., & Williams, H. L. (1992). Dynamic mechanical properties of polypropylene–polyamide blends: Effect of compatibilization. *Journal of Applied Polymer Science*, *44*(4), 699–717.

Narayanan, M., Kandasamy, G., Murali, P., Kandasamy, S., Ashokkumar, V., Nasif, O., & Pugazhendhi, A. (2021). Optimization and production of polyhydroxybutyrate from sludge by Bacillus cereus categorized through FT-IR and NMR analyses. *Journal of Environmental Chemical Engineering*, *9*(1), 104908.

Ritonga, A. H., Jamarun, N., Arief, S., Aziz, H., Tanjung, D. A., & Isfa, B. (2022). Improvement of mechanical, thermal, and morphological properties of organo-precipitated calcium carbonate filled LLDPE/cyclic natural rubber composites. *Indonesian Journal of Chemistry*, *22*(1), 233–241.

Ritonga, A. H., Jamarun, N., Arief, S., Aziz, H., Tanjung, D. A., & Isfa, B. (2023). The Effect of Oleic Acid-Grafted Linear Low-Density Polyethylene as Compatibilizer on the Properties of Linear Low-Density Polyethylene/Cyclic Natural Rubber Blends. *International Journal of Technology*, *14*(1).

Sapsrithong, P., Sritapunya, T., Tuampoemsab, S., Rattanapan, A., & Nithitanakul, M. (2020). Morphology and mechanical properties of polyamide 6 and polybutylene terephthalate blends compatibilized with epoxidized natural rubber. *IOP Conference Series: Materials Science and Engineering*, *811*(1), 12019.