Proceedings

Reclaiming of ground tire rubber by primary and secondary amines as the devulcanizing agents †

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†Presented at Asia Rubber and Elastomer Federation International Conference AREF-IC 2024, AVANI+ Khao Lak, Phang-Nga, Thailand on Feb. 27-Mar.1, 2024.

Abstract:

Recycling end-of-life tires is an environmental challenge due to their high-performance characteristics. In this study, varying amounts of caprolactam and hexamethylenediamine are utilized for the first time to facilitate the devulcanization of rubbers. The primary or secondary amine groups present in caprolactam and hexamethylenediamine can cleavage crosslink bonds, thereby increasing the degree of devulcanization, and sol fraction and decreasing the crosslink density of reclaimed rubbers (RRs). Using 100 phr ground tire rubber (GTR) prepared at 180°C in 75 minutes with processing oil and adding caprolactam and hexamethylenediamine prove that amine groups impacted RRs with different devulcanization degrees. Increasing the amounts of caprolactam exhibits the highest devulcanization degree of 77.7%, surpassing commercial TEPA (70.8%) and exceeding that of thermally devulcanized GTR. However, with hexamethylenediamine, the degree of devulcanization is lower at 58.0%. Torque measurements from MDR show that increasing the amounts of caprolactam and hexamethylenediamine results in lower torque (0.95 and 0.90 dN.m) compared to TEPA (1.19 dN.m). In conclusion, caprolactam, containing the amine with an α-H atom, proves its effectiveness as a devulcanizing agent. However, both caprolactam and hexamethylenediamine have the potential to be devulcanizing agents.

Keywords: caprolactam; devulcanizing agent; hexamethylenediamine; reclaimed rubber; rubber recycling.

1. Introduction

Tires contribute to about 70% of global rubber production and every year, roughly 800 million (~10 million tons) of trash tires are wasted globally (Asaro et al., 2018). Devulcanization of rubber waste is a proposed method of recycling waste tire rubber that involves the cleavage of intermolecular carbon-sulfur and sulfur-sulfur bonds, resulting in

shorter polymer chain lengths than the original, and thus worse rubber characteristics (Thaicharoen et al., 2010). To effectively devulcanize, sulfide compounds, such as diphenyl disulfide, are usually utilized at temperatures of 200°C or higher. This may result in higher energy usage and possible rubber thermal degradation (Guo et al., 2024). Based on the initial patent in 2003 by (van et al., 2003) amines may assist in radical-dominated high-temperature devulcanization.

Hexadecylamine was used by Dijkhuis et al. (Dijkhuis et al., 2008) To devulcanize EPDM during thermal devulcanization, they found a 50% reduction in crosslink density. Tetraethylenepentamine (TEPA), and other amine substances have also been used in conjunction with mechanical or ultrasonic devulcanization, enabling the treatment to be carried out at lower temperatures (Sutanto et al., 2006). Based on this consideration, exploring amine compounds as a devulcanizing agent for rubber reclamation, gave rise to this research idea, caprolactam, and hexamethylenediamine. They are promoted as an innovative devulcanizing agent with the potential to devulcanize waste tire rubber.

The purpose of this study is to investigate the devulcanization mechanism of amine groups of caprolactam and hexamethylenediamine (HMDA) on ground tire rubbers, as well as to optimize the process reattachment after the positively charged sulfur produced by sulfur-breaking is linked with the amine from the devulcanizing agent. This study addresses an effort on a devulcanization process employing amine compounds, focusing on sol fraction and crosslink density, which can directly indicate the degree of devulcanization. This research prioritizes simplicity, employing environmentally friendly sources and chemicals, and minimizing energy consumption.

2. Experimental

2.1 Materials

The materials used in the devulcanization process include tread rubber powders from waste tires (obtained from Union Commercial Development Co., Ltd), the particle size of the rubber powders is mainly distributed 20 mesh. Caprolactam, hexamethylenediamine, and tetraethylenepentamine (TEPA) were purchased from Sigma Aldrich. Alpha-terpineol is a processing oil purchased from beScents.

2.2. Experimental procedure

2.2.1. Devulcanization process

Ground tire rubber (GTR) (100 phr) was combined with 10 phr of processing oil and various concentrations of caprolactam and hexamethylenediamine (5; 10; 15 phr) at room temperature (D-CaproGTRs and D-HMDAGTRs), and for controlling 10 phr of only TEPA was added to GTR (D-TEPAGTR). The devulcanization procedure was then performed for 75 minutes using an internal mixer set to 70 rpm and 180°C. Following devulcanization, the sample was removed from the internal mixer and chilled immediately in a water bath. The sample would next be rolled through the two-roll mill before being compressed (Wang et al., 2023).

2.3 Measurements and Characterizations

The sol fraction was evaluated by Soxhlet extraction (Alonso Pastor et al., 2021). A rubber sample with a certain mass was extracted in acetone for 12 hours, dried at 80°C to a constant weight (m_1), and further extracted in toluene for 16 hours before being vacuum-dried at 80°C to a consistent weight (m_2). The sol fraction is calculated by:

$$S_f = (m_1 - m_2)/m_1 \quad (1)$$

The devulcanizing ratio, which represents the degree of devulcanization, is computed by:

$$Rd = (v_{e1} - v_{e2})/v_{e1} \quad (2)$$

The crosslink density of a rubber sample was determined using the equilibrium swelling method and the Flory-Rehner equation (Shi et al., 2012). The sample was Soxhlet-

extracted in acetone for 12 hours, dried at 80°C to a constant weight (m_i), and then swelled in toluene for 72 hours at room temperature. After removal from toluene, it was weighed (m_t) and dried to a constant weight (m_d) at 80°C. Then, the crosslink density of the rubber sample is calculated by:

$$v_e = \frac{-[\ln(1-V_r) + V_r + \chi V_r^2]}{V_l\,(V_r^{1/3} - V_{r/2}} \quad (3)$$

$$V_r = \frac{m_d/\rho_d}{m_d/\rho_d + m_s/\rho_s} \quad (4)$$

$$m_s = m_t - m_d \quad (5)$$

The torque profile was evaluated by Moving Die Rheometer (CEAST 5000) at 100°C, the sample was prepared at approximately 4.5 cm^3 or at least the minimum size of the cone to cover all the cone and plate surface.

SEM observation with a scanning electron microscope Hitachi S-4800 with an accelerating voltage of 20 kV and EDX mode was performed using the EMAX program. The sample, 1 mm thick, was pre-fractured with liquid nitrogen, attached to a cross-sectional stub using carbon tape, and vacuumed to remove moisture. Sputter-coating was applied for 5 minutes (for non-conductive materials) at a discharge current of 10 to 20 mA to eliminate surface layers or contaminants.

3. Results and Discussion

3.1. Effect of amine-based compounds as devulcanizing agent during the Rubber Reclamation Process

Caprolactam and hexamethylenediamine are two compounds used in this study because they contain primary and secondary amine (Mousavi et al., 2016). It would be compared to Tetraethylenepentaamine (TEPA) which also contains primary and secondary amine (Jiang et al., 2018). Primary and secondary amine were expected to show a high degree of devulcanization and sol content, and lower crosslink density on the ground tire rubber.

3.1.1. Characteristics of Reclaimed Rubbers

Increasing the amount of devulcanizing agent showed increasing the devulcanization degree and sol fraction. **Table 1**, Using (5; 10; and 15 phr) of caprolactam and hexamethylenediamine also get lower crosslink density and the torque profile. For caprolactam, it showed from 5 to 15 phr gives a higher degree of devulcanization approximately 78% than TEPA (70%). On the other hand, using hexamethylenediamine started from 10 to 15 phr gives a higher sol content approximately 8% than TEPA (3%). This, in turn, demonstrated the sol fraction's strong dependency on reclaiming agent content. During devulcanization, GTR experiences massive mechanical shearing in a lower-temperature environment, resulting in random polymer chain breakup (Zhang et al., 2018). A reduced total crosslink density is the consequence of successful devulcanization, which is often shown by a larger sol fraction and lower gel fraction. This is because the crosslinks in the rubber matrix are broken during the devulcanization process, increasing the amount of soluble polymer chains (sol fraction) and decreasing the crosslinked network (gel fraction) (Barbosa & Ambrósio, 2019).

Table 1. Sol-gel fraction, swelling, crosslink, and devulcanizing degree using caprolactam and hexamethylenediamine as a devulcanizing agent.

Sample code	Sol (%)	Gel (%)	Swelling (%)	CLD (10^{-4} mol/cm^3)	DD (%)
DGTR	6.8	93.2	257.9	7.9	50.9
D-Terpineol-GTR	10.6	89.4	262.8	7.3	63.8
D-TEPA-GTR	9.01	90.9	343.2	5.9	70.8
D-Capro5-GTR	14.9	85.1	304.0	5.0	68.9
D-Capro10-GTR	20.3	79.7	271.2	4.9	75.2
D-Capro15-GTR	23.6	76.4	282.0	4.4	77.6
D-HMDA5-GTR	14.4	85.6	238.7	13.2	34.5
D-HMDA10-GTR	16.9	83.1	278.9	9.2	54.1
D-HMDA15-GTR	11.8	88.2	291.6	8.4	58.0

At higher devulcanization degrees, torque decreases due to lower crosslink density. Lower crosslink density is the result of crosslinks breaking during the devulcanization of rubber. Generally, this method softens the material and enhances polymer chain mobility, lowering the torque (Kim et al., 2020). This leads to more effective collisions among molecules and higher devulcanization (**Figures 1**a and b) (Zhang et al., 2009). Figures 1a and b show that the devulcanizing agent can briefly lower the crosslink density and get a high sol fraction.

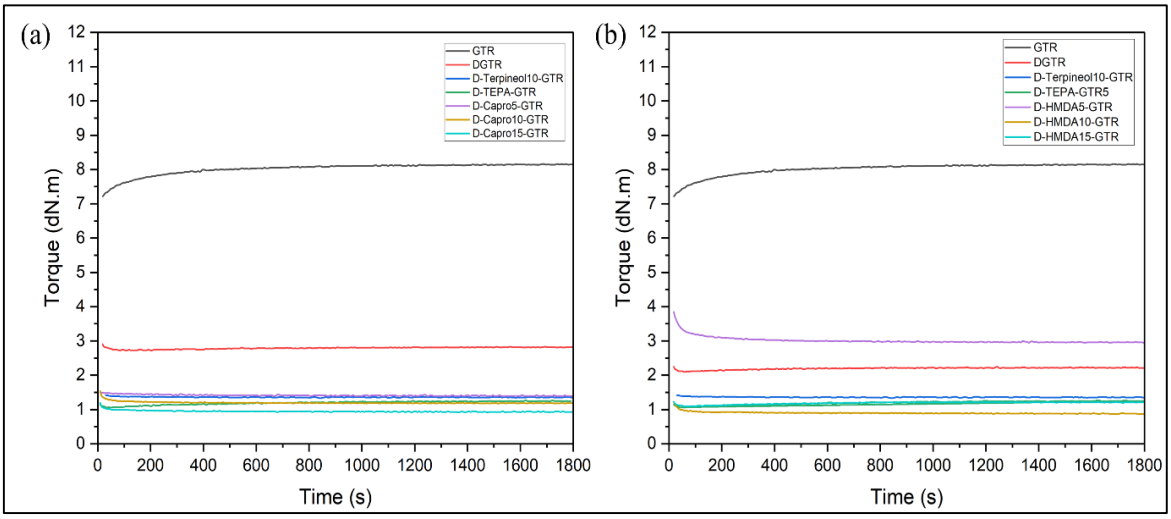

Figure 1. (a) The torque results from using different amounts of caprolactam and (b) hexamethylenediamine.

Figure 2 reveals the contrasting surfaces of GTR before and after adding devulcanizing agents. Incorporating both processing oil and devulcanizing agent into the GTR yields higher sol fraction than GTR, consequently reducing crosslink density. This softening effect is quantified by the decrease in hardness (Shore A), from ±40 for GTR to ±30 after the addition of processing oil and devulcanizing agent. Thus, the observed relationship between sol fraction and sample softness is the inverse correlation.

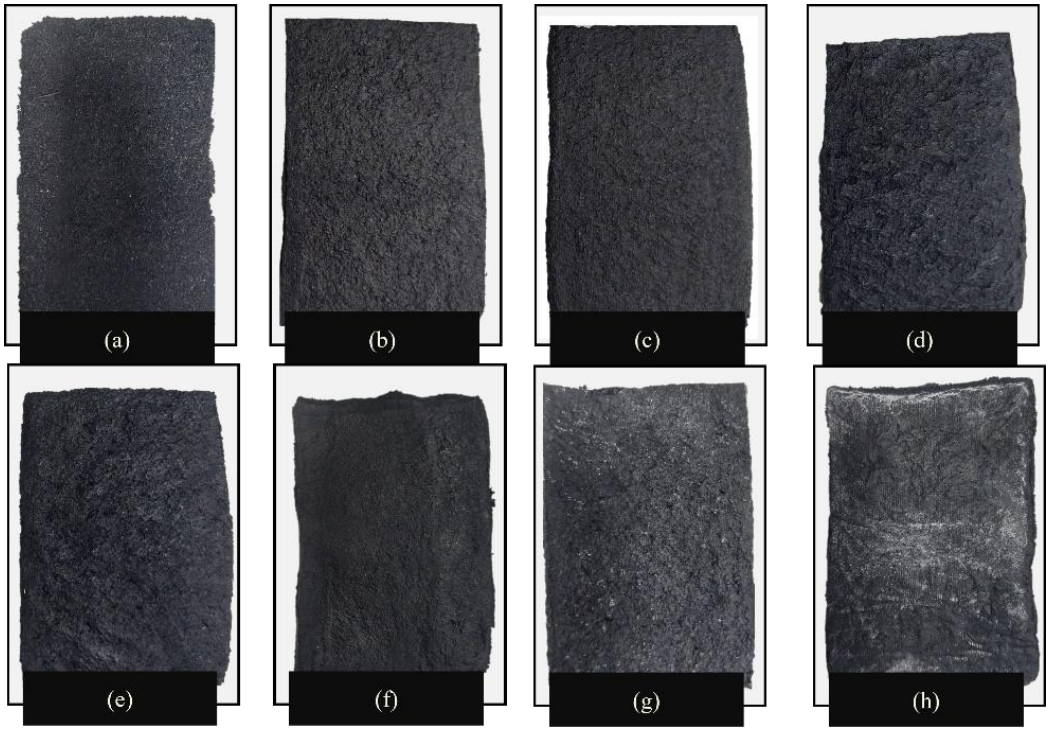

Figure 2. The appearance of the samples; (a) GTR; (b) DGTR; (c) D-Terpineol-GTR; (d) D-TEPA-GTR; (e) D-Capro-GTR; (f) D-HMDA-GTR; (g) D-Capro-GTR (without oil); (h) D-HMDA-GTR (without oil).

3.1.2. Mechanisms between ground tire rubber and caprolactam and hexamethylenediamine

When rubber networks experience high shear, the external force breaks S-S bonds, creating positively charged $-S^{+}$ and negatively charged $-S^{-}$. To prevent the reattachment of charged sulfur atoms, caprolactam and HMDA act as devulcanizing agents. Amine groups from caprolactam and HMDA, with lone pair electrons on their N atoms, attack $-S^{+}$. This process disrupts S-S bonds in rubber networks while preserving rubber macromolecules and attaching them to amine groups in **Figure 3** (Jiang et al., 2018).

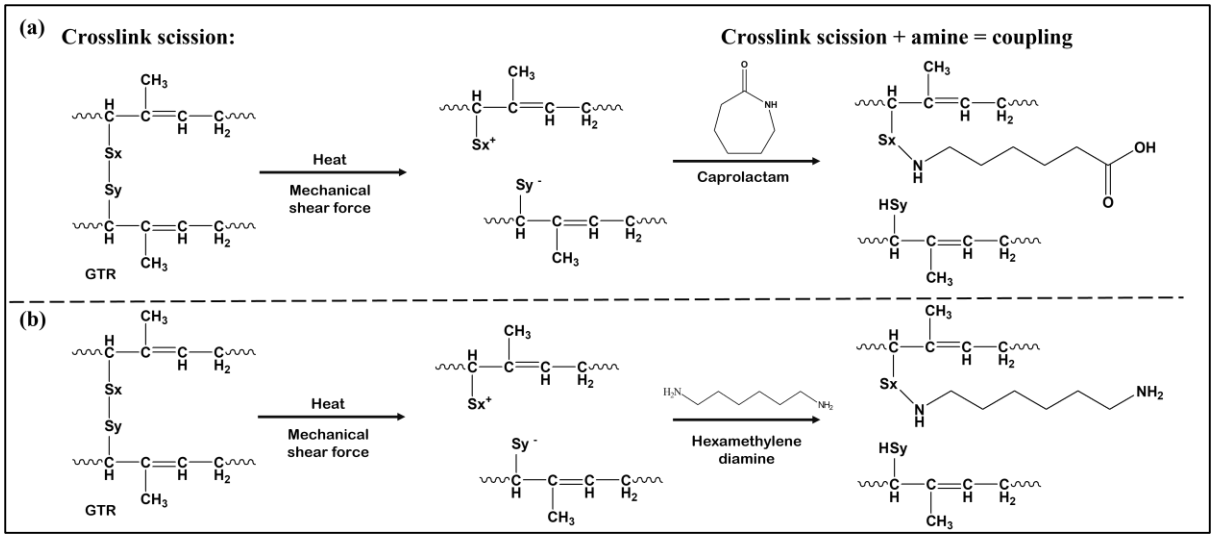

Figure 3. The mechanisms for (a) the mechanism between the secondary amine of caprolactam and ground tire rubber (GTR), and (b) the mechanism between hexamethylenediamine containing secondary amine with GTR.

3.2. SEM-EDX

The microstructure of the raw GTR exhibits a continuous and smooth appearance, suggestive of a homogeneous and cohesive material. Conversely, in **Figure 4,** the picture of devulcanized GTR (DGTR) reveals a granular structure characterized by agglomerates of rubber gels and voids. Upon the addition of caprolactam and HMDA to the GTR, these agglomerates and voids play a significant role in the devulcanization process. In particular, HMDA exhibits a propensity to crystallize at room temperature, corroborated by SEM analysis presented in **Figure 4**(d), illustrating residual particles adhering to the GTR surface. Consequently, HMDA achieves a lower degree of devulcanization compared to caprolactam.

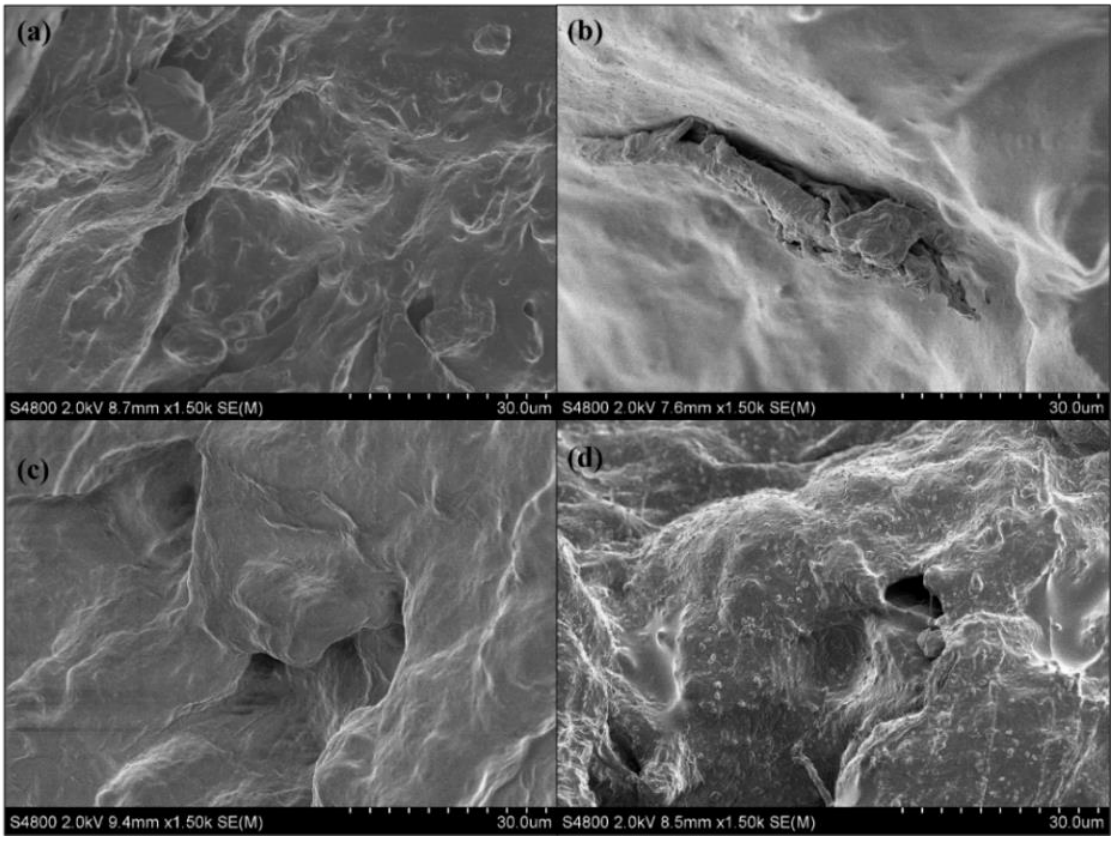

Figure 4. SEM micrograph of (a) DGTR, (b) D-TEPA-GTR, (c) D-Capro-GTR, and (d) D-HMDA-GTR using 10 phr for TEPA, caprolactam, and hexamethylenediamine in GTR.

However, EDX results show the remaining amount of sulfur, during the thermo-devulcanization, S-S bond scission could degrade as sulfur compounds e.g. SO_2 and H_2S as presented in **Table 2**.

Table 2. wt% from EDX of DGTR, TEPA, Caprolactam, and Hexamethylenediamine on the GTR.

Element	**wt%**			
	DGTR	**D-TEPA-GTR**	**D-Capro-GTR**	**D-HMDA-GTR**
C	77.67	50.34	42.03	52.76
N	-	16.12	38.21	18.92
O	19.11	31.05	19.63	25.95
S	3.22	2.48	0.13	2.37
Total	100			

This finding suggests that employing HMDA reduces sulfur degradation rather than caprolactam while preserving the main chain of the GTR. Hexamethylenediamine may also encourage more oxidation reactions since the oxidation is a part of the devulcanization

process which would raise the rubber's oxygen content. Hexamethylenediamine may react with the rubber in a way that promotes the incorporation of ambient oxygen. This may occur as a result of the more efficient exposure of oxygen-containing groups within the GTR of about ±26% (Li & Koenig, 2005). Based on the water content in the reclaiming agents, hexamethylenediamine is higher (±9%) than caprolactam and TEPA about similar in ±2%.

4. Conclusions

In this work, increasing the concentration of amine compounds, employed as devulcanizing agents, effectively enhances the degree of devulcanization and sol fraction while reducing crosslink density. Starting with 5 phr of caprolactam and 10 phr of HMDA yields approximately 75% and 58% devulcanization degree, respectively. EDX analysis shows that caprolactam and HMDA obtained (±3%) of the quantified sulfur content of ground tire rubber. The results provide the great potential of caprolactam and HMDA as devulcanizing agents in the mechano-chemical.

Acknowledgments: The authors would like to express their gratitude to the National Research Council of Thailand (NRCT) and the Scholarship Program for ASEAN or Non-ASEAN Countries at Chulalongkorn University for supporting this research.

Conflicts of Interest: "The authors declare no conflict of interest."

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Effect of Epoxidation Degree on Self-healing Epoxidized Natural Rubber Properties: Cure Characteristics, Mechanical and Abrasion resistance

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Abstract: The present study investigates the effects of two different epoxidation percentages of epoxidized natural rubber (ENR) at 25 (ENR25) and 50 (ENR50) mol% on the cure characteristics, mechanical properties, and self-healability regarding to the healing temperature and time. To achieve the optimized self-healing propagation, ENR was modified with butyl imidazole (IM) and carbon black (CB) to enhance the composites properties. It was observed that the ENR25 and CB of 45 phr had effectively improved the cure properties, in terms of scorch time, cure time and the estimated crosslink density. For the healed composites, this M-ENR25-N45 showed also superior reproducibility on tensile properties owing to the presence of ionic linkages among polarity on ENR and IM molecules. Thus, as a results, the composites can be proposed for future tire and healable products under cost-effectiveness and simply on preparation procedure.

Keywords: Epoxidized Natural Rubber (ENR); Imidazole; Self-healability.

1. Introduction

Natural rubber (NR) has been recognized as a versatile elastomer with various mechanical applications owing to its desirable mechanical properties [1]. However, its susceptibility to damage, such as cracks and cuts, has prompted significant investigation into self-healing materials to extend its life expectancy and durability. One promising avenue involves the incorporation of healing agents, such as imidazole (IM), into epoxidized natural rubber (ENR) composites filled with carbon black (CB).

Hence, rubber composites filled with carbon-based particles were found to be an appealing choice towards the improvement of new materials suitable for tire applications, especially inner liner, and tire treads. Recently, self-healing rubber has been proposed with the movement of positive and negative charges across the cutting interfaces. Moreover, it has been found that a combination of conductive filler in the composite significantly improves the healing behavior of the composites [2,3]. Consideration of self-healing composites for extending the possibilities in tire applications, it is a promising and challenging area of research, aiming to improve the electrical conductivity and durability.

Therefore, a self-healing ENR25 and ENR50 modified with butyl imidazole (IM)the ENR filled with CB. The work aims to provide important insights into the design and optimization of self-healing epoxide natural rubber composites with superior cure time, mechanical and abrasion resistance. The goal is to promote the usage of such composites for tire applications, and it is a promising and challenging area of research.

2. Experimental

2.1 Materials

Epoxidized natural rubbers (ENR) with 25 and 50 mol% of the epoxirane ring on the ENR mainchains were purchased from Muang Mai Guttrie Public Company Limited (Surat Thani, Thailand). In addition, conductive carbon black (CCB) grade Vulcan XC72 were purchased from Cabot Corporation (Pampa, TX, USA). The 1-butylimidazole (IM) was received from Merck KGaA (Darmstadt, Germany). Stearic acid was procured from Imperial Chemical Co., Ltd. (Pathum Thani, Thailand). Zinc oxide (ZnO) and sulfur were manufactured by Global Chemical Co., Ltd. (Samutprakarn, Thailand) and Ajax Chemical Co., Ltd. (Samutprakarn, Thailand), respectively. N-Cyclohexylbenzothiazol-2-sulphenamide (CBS) was purchased from Bos ofticon Limited Partnership (Songkhla, Thailand).

2.2 Preparation of composites

Preparation procedures for the ENR25 and ENR50 composites were carried out according to the formulation shown in Table 1. Initially, the modification of ENR using an internal mixer at 40°C and a rotor speed of 60 rpm was performed. ENR25 and ENR50 were masticated for 2 minutes before adding the activators, with mixing continuing for an additional 2 minutes. The CB was then added and continued mixing for another 4 minutes. IM was introduced into the compound, following with the curatives and the mixing was fixed for the total mixing time of 14 minutes. The compound was sheeted at 160°C using compression molding to obtain the 2 mm crosslinked composites following the rheometer testing. It is noted that the modified ENR25 and ENR50 composites with IM and CB were designated using the code “M-ENR25-N45 and M-ENR50-N45”.

2.3 Cure characterization

Cure characteristics of composites with CB were determined using a moving die rheometer (MDR, Monsanto Co., Ltd., Findlay, OH, USA) following the ASTM D5289. The measurements were performed at a fixed oscillating frequency of 1.66 Hz with 1 arc degree amplitude at 160°C. The T_{c90} is the cure time of the sample and M_H–M_L is the difference between maximal and minimal torques as a function of time.

2.4 Mechanical Properties

Mechanical properties, based on tensile testing following ISO 37 (type 2) were measured using a tensile testing machine (model 3365, Instron® Inc., Massachusetts, USA). To measure self-healing ability, dumbbell-shaped samples were also cut using a sharp razor blade before being pressed into the mold and heated at 160°C for 15 minutes without applying any pressure. The healed samples were measured the mechanical properties under the tensile testing mode as the same condition of the unhealed cases. The healing efficiency (X^*), which is the ratio of the obtained values before (X') and after (X'') healing conditioning, was calculated using Equation (1):

2.5 Abrasion Resistance

Abrasion testing of the composites was conducted to indicate their surface detachment resistance while performing in the Taber tester (Model GT-7012-T, GoTech, Taichung, Taiwan), using a maximum of 5 specimens for each formulation following the ASTM D4060. The samples, approximately 110 mm in diameter with 2 mm of thickness, were polished under a 72 rpm rolling speed for 1000 cycles, and the wear index (WI) was calculated following Equation (2):

3. Results and Discussion

3.1 Cure Characterization

Figure 1 shows the cure curves of M-ENR25-N45 and M-ENR50-N45 by reinforcing with the fixed CB and IM modifying agent. It is clearly seen that both curves had shown the reversion behavior due to the poor thermal stability of the ENR regarding thermo-oxidative degradation. In addition, Table 2 summarizes the cure properties of both composites, and it was found that the composites showed increase of the cure time (T_{c90}) with increasing the epoxide group. This can be attributed to the ENR25 had a higher amount of double bonds compared to ENR50 rubber, which leads to the vulcanization reaction occurring faster. In addition, this is also due to the incorporation of CB into the ENR matrix. This filler enhances the strength and heat conductivity, allowing the rubber to undergo vulcanization reaction faster as well. It is noted that the dispersion and distribution of CB throughout the ENR depend on ENR polarity. With higher polarity, ENR might cause self-interaction, preventing interaction between ENR and CB surfaces. Thus, the dispersion of CB inside the ENR matrix can be reduced with a higher level of the epoxide ring. Therefore, with poor dispersion, thermal expansion through the CB network is limited, resulting in an increased cure time. In addition, the M_H-M_L value of ENR25 rubber surpasses that of ENR50 rubber due to its higher double bond content, leading to increased cross-linking. Additionally, the inclusion of fillers further elevates the M_H-M_L value. This enhancement is attributed to ENR25 rubber's superior interaction with carbon black, stemming from their similar polarities [4].

3.2 Mechanical properties

Mechanical properties in terms of tensile strength, elongation at break and 100% modulus of ENR composites are demonstrated in Figure 2 and summarized in Table 3. In figure 2(a), it was found that in the case of M-ENR25-N45, the tensile strength, elongation at break, and 100% modulus are higher than those of M-ENR50-N45. This is due to ENR25 rubber exhibiting higher crosslink density and better strain-induced crystallization (SIC) behavior compared to ENR50 rubber [5,6]. Additionally, the inclusion of molecularly modified (IM) agents results in grafting of IM molecules onto the rubber chain, inducing attractive forces between the chains, as seen the proposed reaction in Figure 5. Reaction shows reaction of IM molecules and ENR molecular chains which can be generated during mixing inside the internal mixer. This ENR modification causes cation and anion on ENR mainchain which can be reversible after breakage. This may lead to rapid alignment of positively and negatively charged rubber chains during stretching, resulting in enhanced strain-induced crystallization behavior and increased difficulty in slippage, thus resulting in higher tensile strength, elongation at break, and 100% modulus compared to ENR50 rubber [7].

The mechanical properties of reprocessed or recrosslinked composite rubber can be indicated in Figure 2(b) and Table 3. Results show a decrease in tensile strength, elongation at break, and 100% modulus compared to both M-ENR25-N45 and M-ENR50-N45 composites before healing (Figure 2(a)). This decline is attributed to different rate of the self healabiltity of the ionic crosslinking inside both ENR25 and ENR50. Also, with the self-attraction among the functional group on ENR mainchain, lower epoxirane ring might perform better healing rate [7].

Upon analysis of the healing efficiency of composite rubber in Figure 3 and Table 4, results show performance of self repairing in both ENR25 and ENR50 rubbers after breakage [8]. This self recovering is attributed to efficient chemical bond formation through alkylation reactions and the isolation of ionic cluster groups, which align rubber chains and improve healing. Furthermore, M-ENR50-45 rubber exhibits superior self-healing compared to M-ENR25-N45, attributed to IM molecule grafting, enhancing attractive forces between rubber chains, and aiding self-healing surface fusion. Additionally, filler agent improvements in

electrical conductivity and heat conduction enhance chain movement, further improving self-healing efficiency [6].

3.3 Abrasion resistance

Figure 4 shows the Wear index of the composite, where a low wear index indicates excellent wear resistance. It can be observed that the M-ENR25-N45 exhibits the lowest wear index compared to the M-ENR50-N45. This result is attributed to the higher crosslink density of M-ENR25 rubber, which is achieved by adding a modifying agent that adjusts the charge on the rubber molecules. At this stage, grafting IM onto ENR molecular chains can be initiated by the reaction shown in Figure 5, which occurs at the hydroxyl groups due to the epoxirane ring opening. As the hydroxyl groups increase, physical and chemical self-interactions among the ENR chains also increase, which hinders the reaction between IM and ENR. This means that, with a decrease in polarity on the rubber main chain, higher crosslinking propagation can occur during the mixing and compressing processes. Consequently, this facilitates easier movement of the molecules and enhances the self-coordination efficiency of the rubber.

3.4. Figures, Tables and Schemes

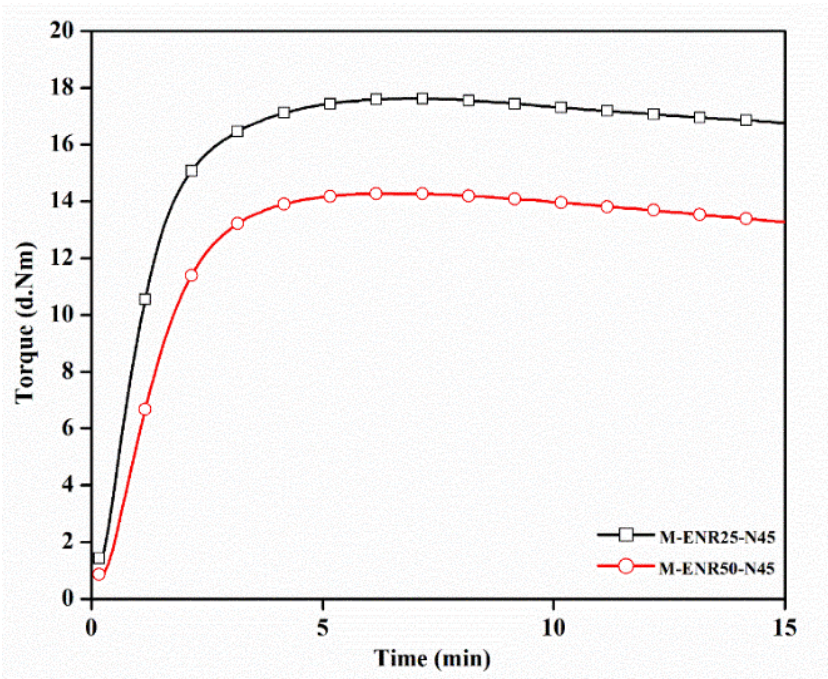

Figure 1. Cure characteristics curves of M-ENR25-N45 and M-ENR50-N45.

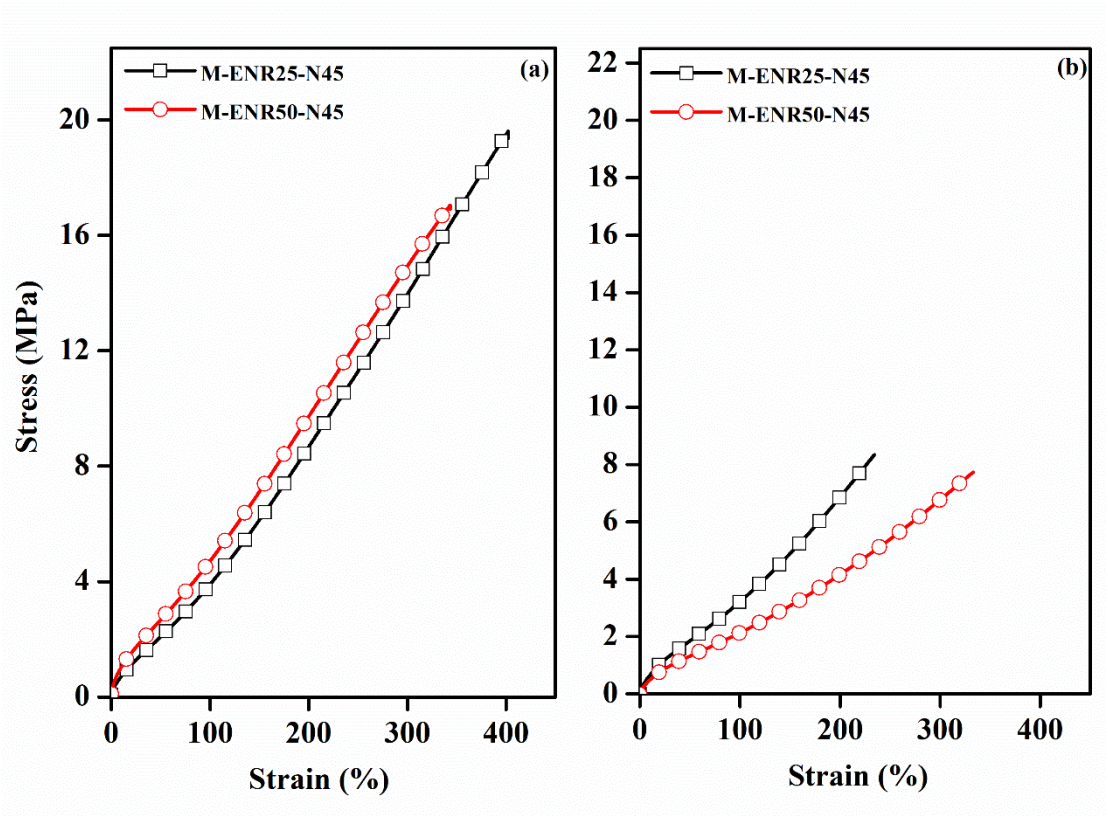

Figure 2. Stress-Strain curves of M-ENR25-N45 and M-ENR50-N45 before (a) and after healing (b).

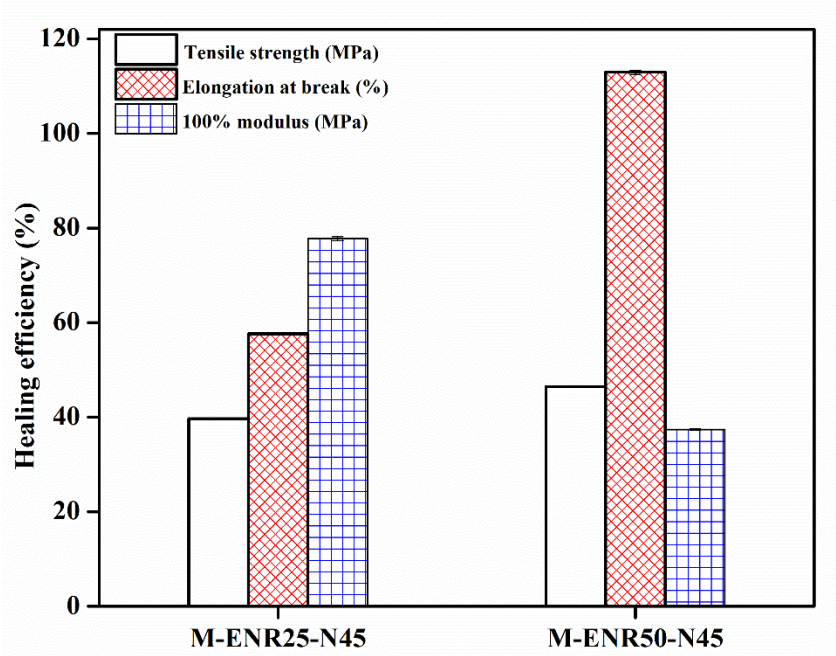

Figure 3. Healing efficiency of M-ENR25-N45 and M-ENR50-N45 based on tensile properties.

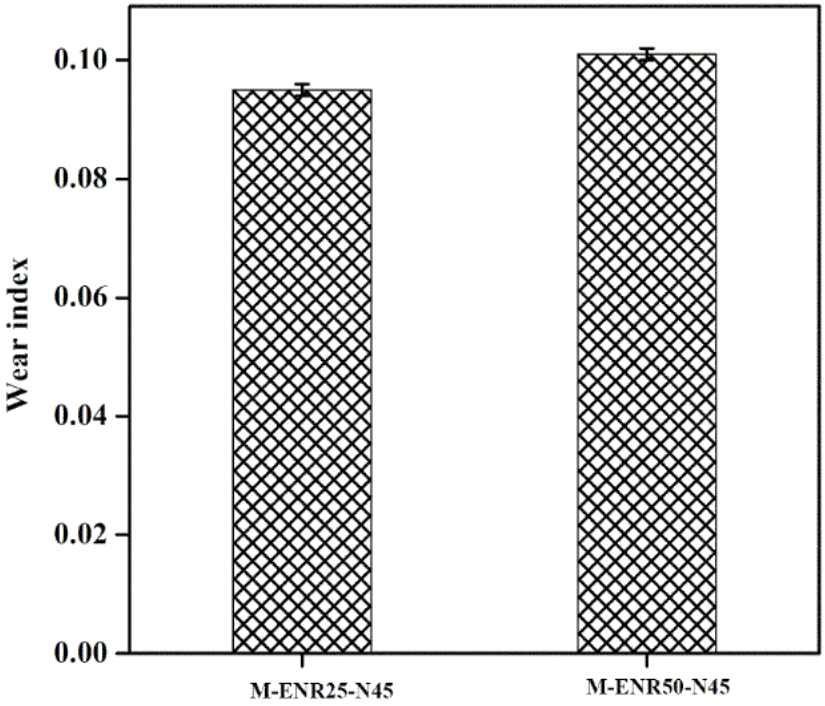

Figure 4. Wear index of M-ENR25-N45 and M-ENR50-N45.

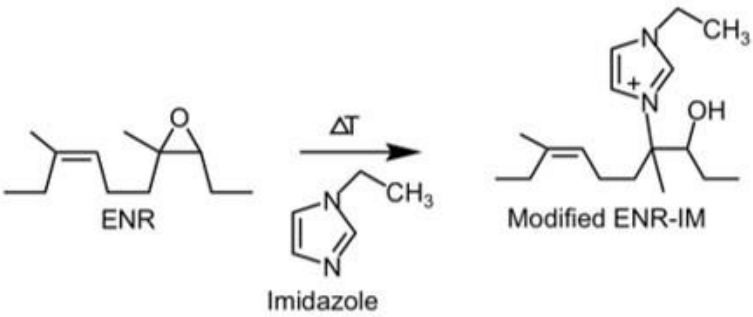

Figure 5. Proposed reaction propagation that occurred during mixing and compressing processes by crosslinking with ENR molecules and IM.

Table 1. Formulation of ENR25 and ENR50 composites.

Ingredients	Chemical roles	Contents (phr)	
		Formula 1	Formula 2
ENR25	Rubber matrix	100	-
ENR50	Rubber matrix		100
IM	Modify agent	5	5
CCB	Filler	45	45
ZnO	Activator	5	5
Stearic acid	Activator	2	2
Accelerator	Accelerator	1.7	1.7
Sulfur	Vulcanizing agent	1.4	1.4

Table 2. Cure characteristics of modified ENR25-N45 and ENR50-N45.

Samples	T_{c90} (min)	M_H (d.Nm)	M_L (d.Nm)	M_H-M_L (d.Nm)
M-ENR25-N45	2.74	17.64	1.42	16.22
M-ENR50-N45	2.92	14.29	0.83	13.46

Table 3. Tensile strength, elongation at break and 100% modulus of composites before and after self-healing propagation.

Samples	Tensile strength (MPa)		Elongation at break (%)		100% modulus (MPa)	
	Before healing	After healing	Before healing	After healing	Before healing	After healing
M-ENR25-N45	19.61±0.04	8.26±0.03	402±0.32	232±0.09	3.91±0.10	3.04±0.09
M-ENR50-N45	17.05±0.03	7.75±0.03	343±0.25	388±0.28	4.71±0.12	1.76±0.06

Table 4. Healing efficiency based on tensile strength, elongation at break and 100% modulus.

Samples	Healing efficiency (%)		
	Tensile strength (MPa)	Elongation at break (%)	100% modulus (MPa)
M-ENR25-N45	42.12±0.12	57.61±0.23	77.75±0.40
M-ENR50-N45	45.45±0.19	112.97±0.45	37.37±0.13

3.5. Formatting of Mathematical Components

$$X^*(\%) = \frac{X''}{X'} \times 100 \quad (1)$$

$$WI = \frac{(W_x - W_y)}{Specific\ gravity} \quad (2)$$

W_x is the weight before loss mass and W_y is the weight after loss mass.

4. Conclusion

The self-healing composites based on modified M-ENR25-N45 and M-ENR50-N45 formulations were studied. The results showed that the M-ENR25-N45 exhibits superior reproducibility in tensile properties due to the presence of ionic linkages among ENR and IM molecules regarding the lowering of the self-crosslinking among the ENR molecular chain owning to high level of polarity of the rubber mainchains. Consequently, these composites are suggested for tire and healable product applications due to their simple preparation procedure.

Author Contributions: P.L.: Conceptualization, Methodology, Validation, Formal analysis, Writing—original draft preparation, T.S.: Conceptualization, Methodology, Validation, Formal analysis, Y.N.: Visualization, Supervision, Formal analysis, Writing—review and editing, Funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Higher Education, Science, Research, and Innovation, grant number RGNS 64-100, and the National Science, Research, and Innovation Fund, grant number B01F640031.

Acknowledgments: This work (Grant No. RGNS 64-100) was supported by the Office of the Permanent Secretary, Ministry of Higher Education, Science, Research and Innovation (OPS MHESI), Thailand Science Research and Innovation (TSRI). Additionally, the National Science, Research, and Innovation Fund (NSRF) via the Program Management Unit for Human Resources and Institutional Development, Research and Innovation [grant number B01F640031] was acknowledged.

Conflicts of Interest: "The authors declare no conflict of interest."

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Proceedings

Life Cycle Assessment of Composite Based on ENR/Wet Blue Leather

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Life Cycle Assessment of Composite Based on ENR/Wet Blue Leather, Breakout Foyer of Koh Tachai and Koh Panyi, 28 February 2024.

Abstract: Wet blue leather scrap from the leather industry is possible to end up in landfills. These have an impact on the environment. The objective of this study is to assess and compare routes between landfills and recycled materials. Environmental impacts include acidification potential, climate change, depletion of abiotic resources - elements, ultimate reserves, depletion of abiotic resources - fossil fuels, eutrophication, freshwater aquatic ecotoxicity, human toxicity, marine aquatic ecotoxicity, ozone layer depletion, photochemical oxidation, terrestrial ecotoxicity. OpenLCA software version 2.1.1 and impact assessment method CML-baseline version 4.4. were used for life cycle assessment in this study. The landfill route shows a higher risk number than the recycled materials route in almost every aspect. Especially freshwater aquatic ecotoxicity, human toxicity, and terrestrial ecotoxicity.

Keywords: Life cycle assessment; recycle; epoxidized natural rubber; composite; leather; wet blue leather.

1. Introduction

Environmental problems are now a global concern. It is estimated that there are approximately 1 billion cattle globally, of which about 300 million are slaughtered each year. Of these, 55% of the hides are turned into leather, while 45% go to waste. This means that 135 million hides per year end up in landfills. Chrome metal is widely used as a tanning agent in

leather production. This chemical substance is known to be carcinogenic and causes environmental pollution.

1.1. Life cycle assessment

Ulya *et al.*[2] studied the life cycle assessment of cow-tanned leather products. The study aims to estimate the environmental impact of cow-tanned leather. In production in Indonesia, the life cycle assessment (LCA) method used was a gate-to-gate perspective to obtain the environmental impact at each stage of cow leather production. The leather tanning industry produces liquid waste and solid waste in its production. As a result, the leather tanning process in Indonesia showed several impact categories, in which marine aquatic ecotoxicity of tanning was the highest concern at the value of 38800 Kg 1,4-dichlorobenzene eq.

1.2. Composite

A composite is something made up of multiple distinct parts or elements. In various contexts, such as materials science, it denotes a material composed of two or more different substances that retain their individual characteristics while contributing to improved performance properties, such as strength or durability, when combined. Li *et al.*[3] found that the effect of triethoxyvinylsilane-modified leather collagen fibers (M-LCF) improves the mechanical properties of the composite. The tensile strength, elongation, and fracture toughness of the NR/M-LCF with 5% modified collagen fibers reached 18.76 MPa, 740%, and 54.09 $MJ \cdot m^{-3}$, respectively. The composite has higher tensile strength, elongation, and fracture toughness than natural rubber. Laurentia *et al.*[4] produced a new biodegradable composite material using post-consumption thermoplastic polyurethane waste (WTPU) compounded with post-consumption finished leather waste (WL). using a double-screw extruder at 1% by weight of polyethylene grafted with maleic anhydride and up to 20% by weight of fiber content. The effect of WTPU showed the reduction of elongation at break, elasticity, and tear strength but an increase in hardness. there is increased hardness. Makes the composite more rigid. However, the tear resistance is more than twofold reduced compared to WTPU. Meyer *et al.*[5] compared the structure and technical performance of shoe upper leather with nine alternative materials,

the coarse fiber bundle mesh layer has the function of high mechanical resistance, tensile strength, and tear strength.

Stefaniak *et al.*[6] showed that phytochemicals from catechin hydrate, eugenol, and flavone could be used as a natural antioxidant for epoxidized natural rubber (ENR) and poly (lactic acid) (PLA) green composites. Surana *et al.*[7] found that adding leather particles 15 wt% increased compressive toughness by 29% of leather/HDPE-epoxy blended composite. Fracture surface analysis showed that the aggregation of small leather particles size 800 μm caused a change in the failure of epoxy from brittle to tough.

1.3. Waste management

Currently, there is an increased demand for vehicles. Resulting in the use of more tires in production and use of vehicles. This directly results in more tire waste, which is waste that is difficult to recycle. Meng *et al.*[8] studied rubber waste management in China and reported that 47.07% of waste is truck tire waste, therefore, switching to a more integrated mix of clean energy could be a good way to reduce the environmental impact of rubber waste. There are ways to recycle rubber waste as follows: Reclaimed rubber production (RRP), rubber powder production (RPP), pyrolysis (PRS), tire retreading (TR), and prototype utilization (PU). Fela *et al.*[9] proposed the leather waste substitution of hard coal for energy recovery. Wan *et al.*[10] showed that the presence of microplastics in landfill waste in the bottom soil varied from 590 to 103080 items/kg and from 570 to 14200 items/kg, respectively.

This study aims to use leather waste, wet blue leather mixed with epoxidized natural rubber (ENR) to make an artificial leather composite. Therefore, the life cycle impacts of wet blue leather discarded in the landfill were assessed and compared to the composites. To analyze the impacts including acidification potential (average Europe), climate change (global warming potential 100-year), depletion of abiotic resources (elements, ultimate reserves), depletion of abiotic resources (fossil fuels), eutrophication (generic), freshwater aquatic ecotoxicity, human toxicity, marine aquatic ecotoxicity, ozone layer depletion (steady state), photochemical oxidation (high oxides of nitrogen, NO_x), terrestrial ecotoxicity. The purpose of this work is mainly to prove that composite could be an optional project to replace landfill route.

2. Experimental

This experiment is performed by openLCA software version 2.1.1. The method used is CML-baseline version 4.4 and database used is LCIA method pack for openLCA nexus by Cristina rodríguez, Claudia di noi, Michael srocka, Andreas ciroth is licensed under a creative commons attribution-sharealike 4.0 international license. Based on work on *www.openlca.org* and various impact assessment models. Permissions beyond the scope of this license may be available at *www.greendelta.com*, database name used in this experiment is *openlca_lcia_methods_1_5_7*.

2.1. Material flow

The experiment starts with defining various components in the material flow format, creating the flow as shown in table 1.

Table 1. Material flows process.

Flow name	Flow type	Reference flow property
Soaking	Product	Mass
Liming	Product	Mass
Fleshing	Product	Mass
Deliming	Product	Mass
Bating	Product	Mass
Pickling	Product	Mass
Chrome Tanning	Product	Mass
Neutralization	Product	Mass
Washing I	Product	Mass
Splitting	Product	Mass
Shaving	Product	Mass
Landfill	Product	Mass
Washing II	Product	Mass
Drying	Product	Mass
Compounding	Product	Mass
Two Roll Mill	Product	Mass
Compression molding	Product	Mass

2.2. Process

The leather production is the main source of wet blue leather waste. The experimental aim is to compare two main routes. The former is “landfill” and the latter “composite”. In each process, an input/output will be specified which consists of raw materials, machinery electricity in each step, and components as shown in Table 2.

Table 2. Process input and output.

Step	Process	Input flow	Amount	Unit	Output flow	Amount	Unit
1	Soaking	Electricity	0.92	kWh	Cowhide, Soaking	138.30	g
		Raw cowhide	138.30	g			
2	Liming	Cowhide, Soaking	138.30	g	Cowhide, Liming	138.30	g
		Electricity	1.54	kWh			
		Glucose	0.30	g			
3	Fleshing	Cowhide, Liming	138.30	g	Cowhide, Fleshing	135.30	g
					Waste (solid)	276.10	g
4	Deliming	Cowhide, Fleshing	676.20	g	Cowhide, Deliming	676.20	g
		Electricity	1.64	kWh			
		Protease enzyme	0.22	g			
5	Bating	Cowhide, Deliming	676.20	g	Cowhide, Bating	676.20	g
		Electricity	1.64	kWh			
6	Pickling	Cowhide, Bating	676.20	g	Cowhide, Pickling	676.20	g
		Electricity	3.43	kWh			
7	Chrome Tanning	Cowhide, Pickling	676.20	g	Cowhide, Wet Blue	298.20	g
		Electricity	7.84	kWh			
8	Neutralization	Cowhide, Wet Blue	298.20	g	Cowhide, Neutralization	298.20	g
		Electricity	0.22	kWh			
9	Washing I	Cowhide, Neutralization	298.20	g	Cowhide, Washing	280.20	g
		Electricity	0.19	kWh			
10	Splitting	Cowhide, Washing	298.20	g	Cowhide, by-product	149.20	g
		Electricity	1.01	kWh	Cowhide, Splitting	149.20	g
11	Shaving	Cowhide, Splitting	149.20	g	Cowhide, Shaving	149.20	g
		Electricity	0.26	kWh	Cowhide, solid waste	8.04	g
Route 1	Landfill	Cowhide, Shaving	400.00	g	Landfill of textiles	400.00	g
Route 2	Washing II	Cowhide, Shaving	150.00	g	Wet Blue Leather (pass washing)	150.00	g
	Drying	Electricity	1.00	kWh	Wet Blue Leather (Pass oven)	150.00	g
		Wet Blue Leather (Pass washing)	150.00	g			
	Compounding	Wet Blue Leather (Pass oven)	150.00	g	Compound (Pass compounding)	400.00	g
		Epoxidized natural rubber (ENR)	250.00	g			
		Electricity	1.00	kWh			
	Two Roll Mill	Compound (Pass compounding)	400.00	g	Compound (Pass two roll mill)	400.00	g
		Electricity	1.00	kWh			
	Compression molding	Compound (Pass two roll mill)	400.00	g	Composite based on ENR/Wet blue leather	400.00	g
		Electricity	1.00	kWh			

2.3. Product systems

Create a product system of landfill route and composite route by linked various processes as shown in figure 1.

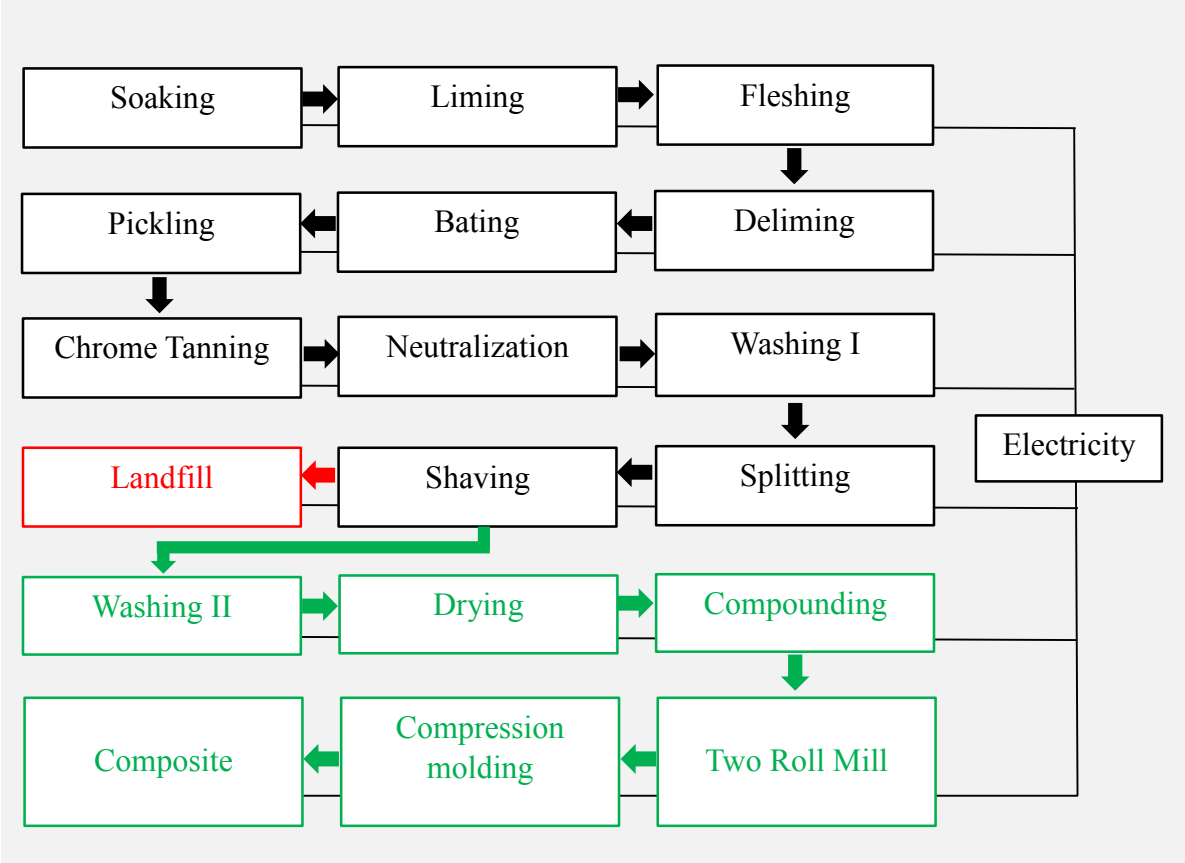

Figure 1. Product systems.

2.4. Project

It is an environmental impact comparison step between the product system of the landfill route and composite route using the impact assessment method CML-baseline version 4.4. to display impact categories.

3. Results and Discussion

3.1. Impact on environment

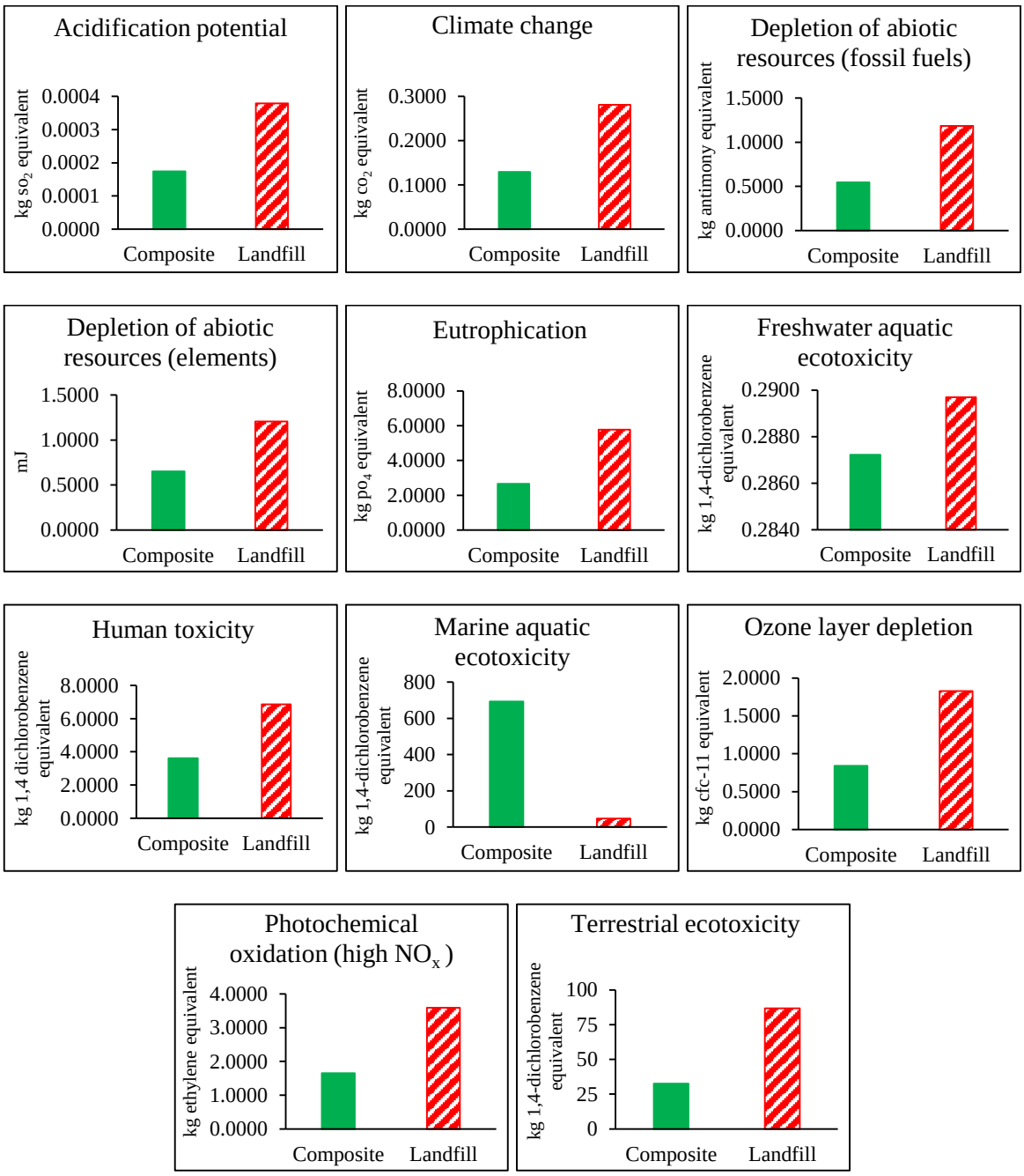

Figure 2. Impact categories comparison.

119 **Table 3.** Life cycle assessment of composite and landfill routes.

Impact Categories	Composite	Landfill	Unit
Acidification potential (average Europe)	0.0002	0.0004	kg so_2 equivalent
Climate change (Global Warming Potential 100-year)	0.1295	0.2808	kg co_2 equivalent
Depletion of abiotic resources (elements, ultimate reserves)	0.6511×10^{-5}	1.2054×10^{-5}	kg antimony equivalent
Depletion of abiotic resources (fossil fuels)	0.5454	1.1852	mJ
Eutrophication (generic)	2.6570×10^{-5}	5.7735×10^{-5}	kg po_4 equivalent
Freshwater aquatic ecotoxicity	0.2872	0.2897	kg 1,4-dichlorobenzene equivalent
Human toxicity	3.6207	6.8614	kg 1,4 dichlorobenzene equivalent
Marine aquatic ecotoxicity	694	47	kg 1,4-dichlorobenzene equivalent
Ozone layer depletion (steady state)	0.8409×10^{-10}	1.8273×10^{-10}	kg cfc-11 equivalent
Photochemical oxidation (high oxides of nitrogen, NO_x)	1.6530×10^{-5}	3.5918×10^{-5}	kg ethylene equivalent
Terrestrial ecotoxicity	33	87	kg 1,4-dichlorobenzene equivalent

120

121 In figure 2 and table 3, composites and landfill routes were successfully analyzed by
122 openLCA software using the CML-baseline method. The environmental impacts of composite
123 and landfill are as follows: acidification potential 0.0002 and 0.0004 kg SO_2 eq., climate change
124 0.1295 and 0.2808 kg CO_2 eq., depletion of abiotic resources (elements) 0.6511×10^{-5} and
125 1.2054×10^{-5} kg antimony eq., depletion of abiotic resources (fossil fuels) 0.5454 and 1.1852
126 mJ, eutrophication (generic) 2.6570×10^{-5} and 5.7735×10^{-5} kg PO_4-eq., freshwater aquatic
127 ecotoxicity 0.2872 and 0.2897 kg 1,4-dichlorobenzene eq., human toxicity 3.6207 and 6.8614
128 kg 1,4-dichlorobenzene eq., ozone layer depletion 0.8409×10^{-10} and 1.8273×10^{-10} kg cfc-11
129 eq., photochemical oxidation (high NO_x) 1.6530×10^{-5} and 3.5918×10^{-5} kg ethylene eq.,
130 terrestrial ecotoxicity 33 and 87 kg 1,4-dichlorobenzene eq., respectively. Except for impacts

on the marine aquatic ecosystem. The composite route had 694 kg 1,4-dichlorobenzene eq., which was higher than the landfill route with 47 kg 1,4-dichlorobenzene eq.

3.2. *Relative result*

Relative result: This is found by dividing the amount of impact on each side of the two wet blue leather management routes by the maximum amount of that impact and multiplying by 100 to get the relative result in percentage form, as shown in figure 3. The composites route has resulted in environmental impacts in acidification potential, climate change, depletion of abiotic resources (elements), depletion of abiotic resources (fossil fuels), eutrophication (generic), freshwater aquatic ecotoxicity, human toxicity, ozone layer depletion, photochemical oxidation (high NO_x), and terrestrial ecotoxicity. It has less impact than the landfill route. It is only in the impact on marine aquatic ecosystems that the composites route has a higher impact than landfills.

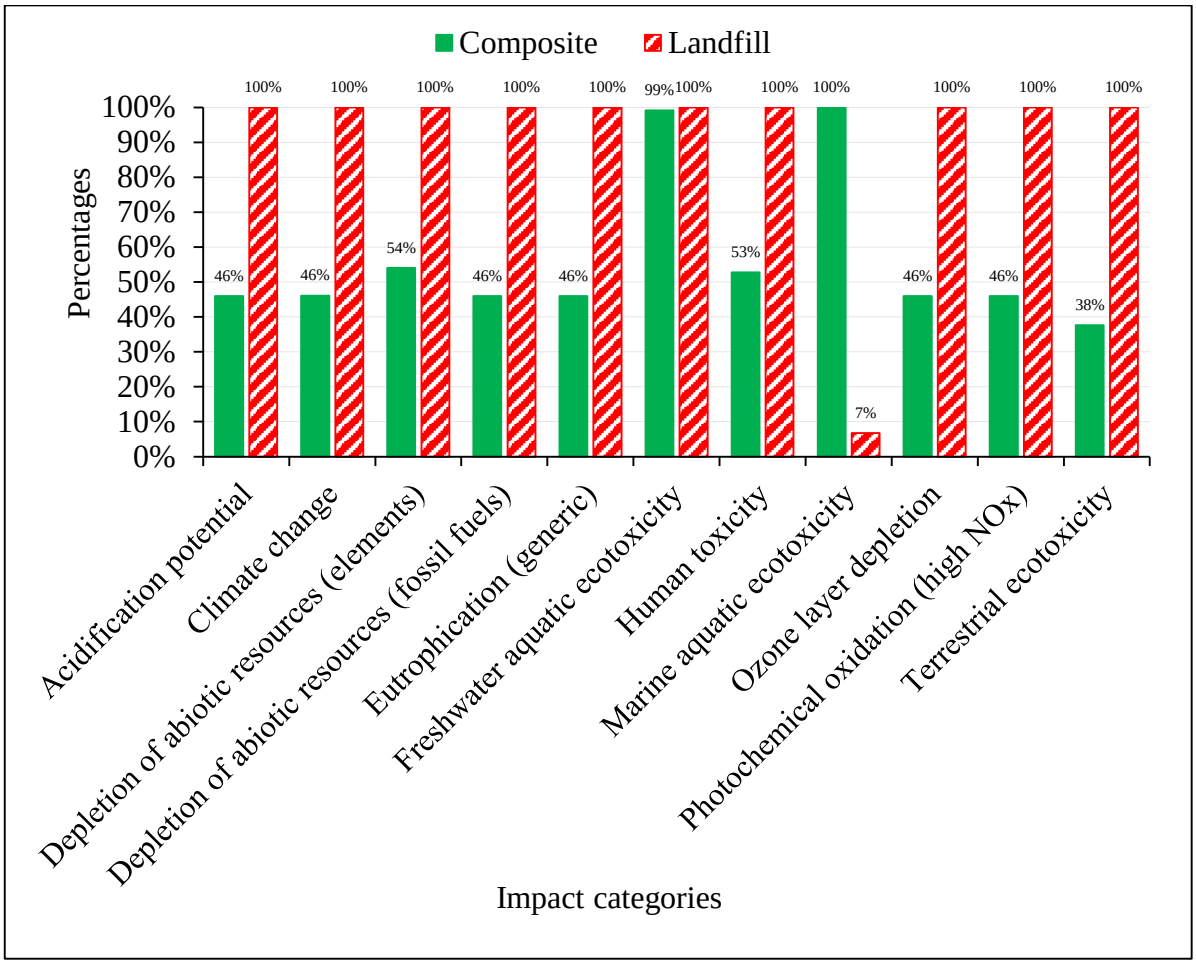

Figure 3. Relative result of life cycle assessment of composite based on ENR/wet blue leather.

Conclusion

The life cycle assessment of wet blue leather on the route between the landfill and composites was successfully analyzed by openLCA software using the CML-baseline method. The results concluded that the composite route from epoxidized natural rubber/wet blue leather has a lower impact than the landfill route in almost every aspect except the marine aquatic ecotoxicity. Therefore, the composite route should be a more suitable alternative to landfill.

Worachai Techo: Methodology, software, draft preparation, formal analysis, investigation, visualization. **Laksamon Raksaksri:** Conceptualization, validation, writing—original, editing, supervision, project administration. All authors have read and agreed to the published version of the manuscript.

Funding: NRIIS number 179334 and grant no. FF7-710-64-36-24(F).

Acknowledgments: This work was supported by Suranaree University of Technology (grant no. FF7-710-64-36-05(F), Thailand Science Research and Innovation (TSRI), and National Science, Research, and Innovation Fund (NSRF) (NRIIS number 179334) (grant no. FF7-710-64-36-24(F)).

Conflicts of Interest: "The authors declare no conflict of interest."

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Effect of modified clay with zinc stearate on properties of natural rubber composites: Cure characteristics, mechanical properties and Payne effect

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Abstract: Natural rubber (NR) composites filled with unmodified and modified clay with chemical formation of zinc ions and stearic acid, namely zinc stearate, were prepared using an internal mixer and a two-roll mill. The intrinsic properties of both clay types were characterized through particle size analyzer and x-rays diffraction (XRD), while the cure characteristics, mechanical properties and storage modulus following the Payne effect were reported after the incorporation inside the NR matrix. It was found that the use of modified clay showed the smaller particle size with exfoliation structure due to the increase band gap among the clay layers. This causes well dispersion of modified clay within NR which further induced chemical crosslinking reaction together with the comparable tensile properties and Payne effect. This means the modification is successfully prepared and the improved properties are established.

Keywords: Natural rubber; modified clay; Dispersion; Payne effect; Properties

1. Introduction

Nanomaterials in the rubber industry have attracted considerable attention as reinforcing agents for elastomeric materials due to their outstanding improvements in various properties compared to traditional composites. In addition to commonly used materials like carbon black and silica, nanoclays are among the most widely utilized and extensively studied fillers. Most commonly used nanoclays in polymers, such as montmorillonite, have a layered structure, discovered by Dumour and Savetat [1]. Currently, it is popular to use nanoclays as reinforcing agents in polymers due to their abundant natural availability and low cost. The prominent feature is their platelet shape with a high aspect ratio and a nanosize thickness, resulting in a high surface area. For this reason, polymers reinforced with nanoclays can improve properties of mechanical, dynamic, adhesion, flame retardancy [2], gas permeability, and thermal stability [3]. However, making a nanoclay composite without modification does not significantly impact natural rubber (NR) because the surface of nanoclay tends to be hydrophilic [4], whereas NR is a hydrophobic polymer. This mismatch may result in poor dispersion and agglomeration within the rubber matrix.

Nevertheless, NR remains a highly appealing material due to its environmental friendliness and outstanding performance characteristics, including resilience, elasticity, abrasion resistance, efficient heat dispersion (minimizing heat build-up under friction), and impact resistance [5]. To enhance dispersion in the rubber matrix, the most commonly used

technique is the cation exchange surface modification method. This process involves exchanging ions between layers with organic cations, leading to the separation of clay platelets, and allowing for easier intercalation and exfoliation. By exchanging of sodium cations for organic cations (surfactants), the interlayer spacing expands [6], resulting in improved dispersion, mechanical properties, and other characteristics. Sookyung *et al.* prepared NR composites filled with octadecylamine-modified montmorillonite nanoclay (OCMMT) using melt mixing processes. It was found that the modified clay improved dispersion and distribution of clay inside NR matrix which further enhanced the degree of rubber chains crosslinking and mechanical properties of the composites. Also, comparing the NR/OCMMT nanocomposites with the unmodified clay, thermal stability and swellability were significantly reduced due to good dispersion of silicate layer in rubber matrix [7]. In addition, Hrachová *et al*. prepared NR nanocomposites filled with organoclay modified using octadecyl trimethylammonium bromide (ODTMA) and the results showed improvement of the mechanical properties in terms of tensile strength, elongation at break, tensile modulus, and hardness. The dispersion of clay within the NR matrix indicated the intercalated and exfoliated of an individual silicate layers [8]. Therefore, the use of modified clays has a positive effect on the properties of rubber composites. The improved dispersion and interaction of modified clays within the matrix enhanced mechanical properties, thermal stability, and dynamic mechanical properties. These enhancements make the modified clay-filled rubber composites suitable for a wide range of industrial applications.

The present research work is aimed to investigate the influence of unmodified clay and modified clay with zinc stearate with natural rubber composites, on the properties of cure characteristics, mechanical properties, and the Payne effect.

2. Experimental

2.1 Materials

Natural rubber (NR), grade STR5L (Standard Thai Rubber 5L), 1,2-Dihydro-2,2,4-trimethylquinoline (TMQ) and N-Cyclohexylbenzothiazol-2-sulphenamide (CBS) were purchased from Bossoftical Public Company Limited (Songkhla, Thailand). ULTRASIL VN23 Silica and silane coupling agent TESPD were obtained from Evonik Industries AG (Wesseling, Germany). Modified clay is the modification of the bentonite clay with zinc stearate using the technique of cation exchange involves replacing Na^+ ions in the clay with Zn^{2+} ions from modifier. Zinc oxide (ZnO) and sulfur were provided by Global Chemical Company Limited (Samut Prakan, Thailand). Stearic acid was purchased Imperial Chemical Company Limited (Pathum Thani, Thailand). Diphenylguanidine (DPG) was purchased Shenyang Sunnyjoint chemicals Company Limited (Liaoning, China).

2.2 Preparation of the NR composites

Preparation process of the NR composites filled with unmodified and modified clay was initiated by the mastication of NR inside an internal mixer in order to reduce the viscosity and surface tension of the NR matrix before adding other chemicals following the Table 1 following the published tire thread formulation. The total mixing operation was carried out for approximately 12 min. The compounds were then passed on the two-roll mill for improving the dispersion and distribution of the unmodified and modified clay throughout the

NR matrix. The NR composites were eventually pressed through the compression molding following the rheometer testing.

2.3 Particle size

The particle size distribution (PSD) of the unmodified and modified clay powder was determined by a Partica LA-960 (HORIBA Limited, Kyoto, Japan).

2.4 X-ray diffraction

X-ray diffraction (XRD) was performed on dried powder samples. The XRD patterns were obtained using a Smart Lab SE (Rigaku Corporation, Tokyo, Japan) with Cu Kα radiation (λ = 1.54 Å). The samples were scanned at a rate of 0.05°/min from 5° to 30° of 2θ.

2.5 Cure characteristics

Curing parameters, including scorch time (t_{s2}), optimum cure time (t_{90}), maximum and minimum torque (M_H, M_L). The compounds were studied using the Rubber Process Analyzer model RPA2000 (Alpha Technologies, Ohio, USA) at 150°C for 30 min.

2.6 Tensile properties

The tensile properties of NR composites filled with unmodified and modified clay were determined using a universal testing machine (Zwick Z 1545, Zwick GmbH and Co. KG, Ulm, Germany). Tests were carried out according to ISO 037 (Type 2), using a 500 N load cell and 200 mm/min crosshead speed.

2.7 Payne effect

The Payne effects of NR composites filled with unmodified and modified clay were evaluated using a RPA200 at a temperature of 100°C, frequency of 1 Hz and varying strains in the range of 0.56– 100%.

3. Results and discussion

3.1 Particles size and interaction among the clay layers

Table 2 shows the average particles sizes of the unmodified and modified clay using the chemical combination of the zinc ion (Zn^{2+}) and stearic acid. It is seen that the combination of the bentonite clay with modifier represented the smaller of the particle size than the one without modification for approximately 2 times. This can be referred to the increase of the distance among the clay layer regarding the penetration of the Zn^{2+}-stearic acid linkages. This clarifies through the demonstration of the XRD results seen in Figure 1. Considering of the appearance peaks among 2θ of 20-30° which assign to the reflection of the X-rays radiation through the clay layer, it is seen that the modified clay exhibited smaller of each peak than the unmodified which disappeared at the 2θ of 20-25°. This means that the clay layer had distance in a proper position which X-ray diffraction cannot be detected. In addition, the XRD pattern of unmodified clay shows a highest peak at a 2θ angle of 7°, corresponding to an interlayer spacing of 1.26 nm. In contrast, the modified clay shows a highest peak at a 2θ angle of 6°, corresponding to an interlayer spacing of 1.48 nm. This indicates that the interlayer spacing

of the modified clay is greater than that of the unmodified clay, confirming the intercalation of zinc stearate into the clay layers.

3.2 Cure characteristics

Figure 2 presents the cure curves of the NR composites filled with unmodified and modified clay. It is clearly seen that both curves show the reversion behavior due to the poor thermal stability of the NR regarding thermos-oxidative degradation. However, the addition of the modified clay slightly retarded the reversion due to the dispersion and distribution of clay within the NR matrix. In addition, Table 3 summarizes the cure properties of both composites, and it was found that the composites showed increase of the scorch time (T_{s2}) and cure time (T_{90}) after using the modified clay. This was explained by the thermal insulation of the clay layers which prevent thermal expansion inside the NR matrix and therefore the vulcanization propagation was slower since the modified clay had better dispersion degrees. Additionally, the higher M_H-M_L, which is assigned to the estimated crosslink density inside the bulk NR composites, is due to the zinc ions released from zinc stearate. These ions facilitate the crosslinking reaction by coordinating with sulfur atoms, thereby promoting their interaction with the rubber chains. This coordination allows for more efficient bonding between adjacent rubber molecules regarding the roles of zinc stearate which can act as the plasticizer for clay dispersion and also activator for increasing crosslink density.

3.3 Mechanical properties and Payne effect

The mechanical properties, including tensile strength, 100% and 300% moduli, and elongation at break of the NR composites filled with different types of clays, are demonstrated in Figure 3, Figure 4 shows the Payne effect and summarizes the data in Table 4. It is seen in Figure 3 that the well dispersion and distribution of the modified clay relative the unmodified clay caused improved significantly the improved 100 and 300% moduli. This means that the composites had high potential to retard the stress applying deformation due to superior reinforcement efficiency. Also, considering the tensile strength (T.S.) and elongation at break (E.B.) of the NR composites, it was observed that the uses of the modified clay provide increase of the T.S. with lower E.B. This correlates to the explanation that the incased tensile strength and stiffness can lower than elasticity of the NR matrix and therefore the E.B. had decreased. Also, it is seen that the NR composites with modified clay showed lower of the Payne effect which mainly referred to the smaller of the clay agglomeration inside the NR composites. Zinc stearate, acting as a clay modifier, reduces friction between the rubber matrix and filler materials, such as clay particles. This friction reduction facilitates better clay dispersion and distribution within the rubber matrix, thereby enhancing mechanical properties.

3.4. Figures and Tables

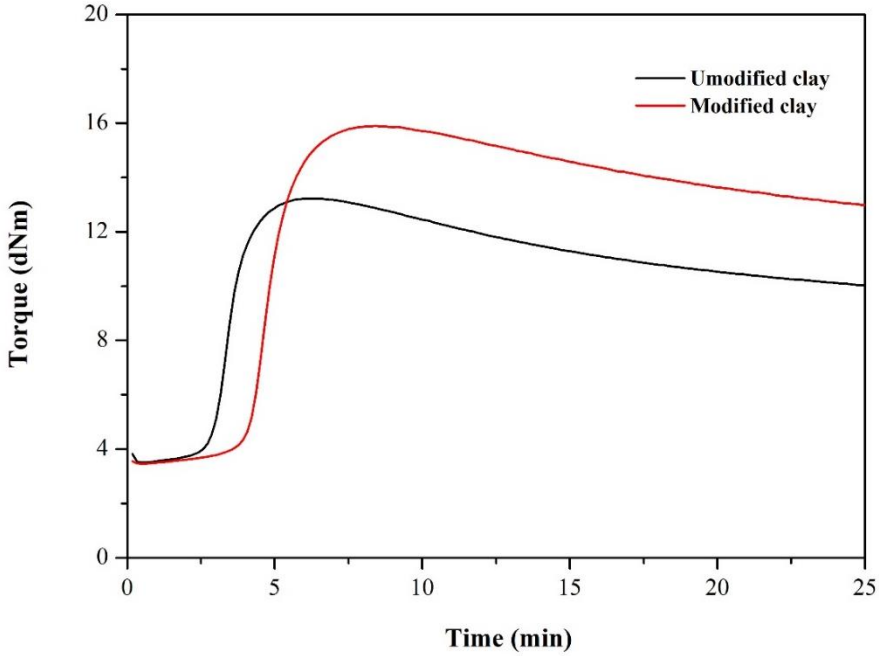


Figure 1 The X-ray diffraction (XRD) patterns of unmodified and modified clay to clarify the distribution of clay particles.

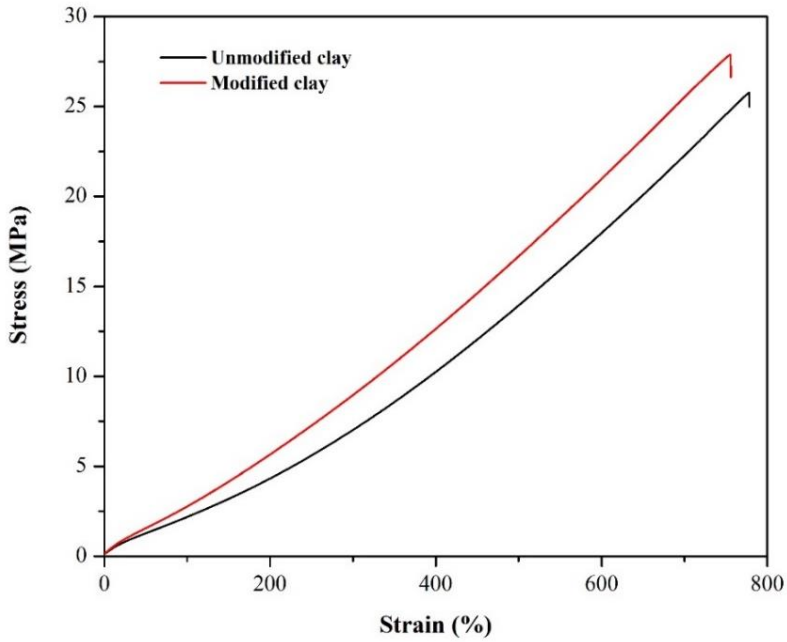
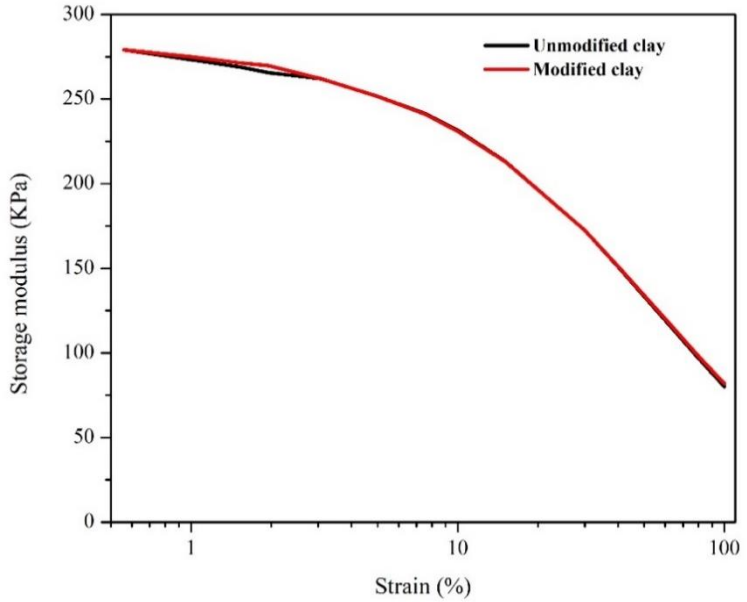


Figure 2 Cure curves of the NR composites filled with unmodified and modified clay.
Figure 3 Stress-strain curves of the NR composites filled with unmodified and modified clay.
Figure 4 Payne effect of the NR composites filled with unmodified and modified clay.

Table 1 Formulation of the NR composites filled with unmodified and modified clay.

Ingredients	Content (phr)
Natural rubber	100
Silica+TESPT	60
Clay/Modified clay	10
ZnO	3
Stearic acid	1
Antidegradant	1
Accelerator	2.6
Sulfur	1.5

Table 2 Particle size of the unmodified and modified clay.



Name	Particle size (μm)
Unmodified clay	8.65
Modified clay	4.01

Table 3 Cure characteristics of the NR composites filled with unmodified and modified clay.

Cure characteristics	NR composites filled with unmodified and modified clay	
	Unmodified clay	Modified clay
T_{s2} (min)	3.10	4.43
T_{90} (min)	4.44	6.21
M_H (dNm)	13.23	15.90
M_L (dNm)	3.50	3.46
M_H-M_L (dNm)	9.73	12.44

Table 4 Tensile properties with the indication of the Payne effect of the NR composites filled with unmodified and modified clay.

Mechanical properties	NR composites filled with unmodified and modified clay	
	Unmodified clay	Modified clay
Tensile strength (MPa)	25.78 ± 0.54	27.89 ± 0.12
Elongation at break (%)	778.25 ± 9.72	755.53 ± 10.26
100 % Modulus (MPa)	2.19 ± 0.03	2.77 ± 0.03
300 % Modulus (MPa)	7.02 ± 0.08	8.96 ± 0.07
Payne effect (KPa)	199.27	197.34

4. Conclusion

The NR composites filled with unmodified and modified clay were carried out by focusing on the improved properties of the NR composites regarding the cure characteristic, mechanical properties, and Payne effect for examining the dispersion and distribution of the clay inside the NR matrix. It was found that the modification of the clay layer with the chemical coupling among Zn^{2+} and stearic acid had smaller of the particle sizes and higher distance among the clay layers. This achievement causes the higher of the crosslinking density for the covalent bonding among the NR molecules and also the modulus and tensile strength of the NR composites relative to the one with unmodified clay. Although the elongation at break was slight lower, the Payne effect showed that improved dispersion of the clay can be gained after the modification process. Therefore, the present work can further apply for the rubber manufacturing which would use the clay as the secondary filler in order to improve the properties of the composites.

Author Contributions: M.M.: Conception and Design, Methodology, Validation, Data Analysis, Writing—original draft preparation, R.M.N.: Conceptualization, Methodology, Validation, Formal analysis, Y.N.: Visualization, Supervision, Formal analysis, Writing—review and editing, Funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research project is supported by King Mongkut's University of Technology Thonburi (KMUTT), Thailand Science Research Innovation (TSRI) and National Science, Research and Innovation Fund (NSRF) Fiscal year (2024).

Acknowledgments: The authors gratefully acknowledge the financial support from the King Mongkut's University of Technology Thonburi (KMUTT), Bangkok, in the form of KMUTT Research Fund for the financial support and equipment. Also, Thailand Science Research and Innovation (TSRI) and National Science, Research and Innovation Fund (NSRF) Fiscal year 2024 was acknowledged.

Conflicts of Interest: "The authors declare no conflict of interest."

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Food-contact potential of polylactic acid/natural rubber (PLA/NR) packaging films

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Abstract:
This research investigated the food-contact potential of polylactic acid/natural rubber (PLA/NR) packaging films at NR contents ranging from 0-25 wt% in terms of chemical migration from the films. The overall migration test was studied by immersing samples in four different food simulants – ethanol 10% (v/v), acetic acid 3% (w/v), ethanol 95% (v/v), and vegetable oil – under both short-term and long-term food contact conditions (OM0 and OM2). The specific migration test was studied using an ED-XRF technique to identify a specific migrant in ethanol 95% (v/v). VOCs that migrated from the films were identified using HS/GC-MS. The result indicated that the PLA/NR films at all NR contents had overall migration amounts well below the EU-regulated standard migration in all food simulants. Chemical analysis revealed the presence of $CaCO_3$ (used as a nonstick agent for NR). According to the VOCs test, No VOCs were released when the PLA/NR films were incubated at 40 °C. This result suggested that PLA/NR films at NR contents up to 25%wt could be used for food packaging applications for all types of food at short and long storage times at cold and ambient temperatures.

Keywords: PLA/NR film; Food contact; Migration test; Overall migration; Specific migration

1. Introduction

Plastic production has grown faster than any other material since 1970s. If the current trend continues, primary plastic production could reach 1,100 million tonnes by 2050. About 36% of those are used for packaging, which includes single-use plastics for food and beverage containers. Almost 98% of these single-use plastics are made from fossil fuels. After being disposed of, around 85% of this plastic ends up in landfills or as unregulated waste[1]. Although many countries promote the use of bio-based plastics as a replacement for petroleum-based plastics, the high production costs remain a challenge. According to 2021 statistics, biodegradable plastics comprised only 1.5% of the world's plastic production and 2.3% of Europe's plastic production[2]. Polylactic acid (PLA) is the cheapest bio-based plastic that has been approved for food packaging[3], [4]. However, it has limitations in terms of its toughness, brittleness, and thermal stability[5]. To enhance its toughness, PLA has been blended with bio- or petroleum-based plastics[6]. Our research group extensively investigated on the blends of PLA and natural rubber (NR) for packaging applications because NR is a fully biopolymer with outstanding elasticity, tensile strength, and toughness. Even though NR is cheaper than PLA, packaging films made from PLA/NR still have a higher cost than petroleum-based plastics. Therefore, it is of interest to expand the application ranges of PLA/NR to food-contact applications. So far, there is a lack of studies investigating the food contact potential of PLA/NR films in terms of consumer safety. Therefore, the food-contact potential of PLA/NR blends could be a challenge and is worth investigation.

2. Experimental

Materials

PLA Pellets 4043D was purchased from Nature Works Co. Ltd., USA. Natural Rubber (STR grade 5L) was purchased from Innovation Group (Thailand) Ltd. Ethanol (95%) (a food simulant) and $CaCO_3$ were purchased from Chemipan Corporation Co., Ltd. Acetic acid (≥ 99.7%) (a food simulant) was purchased from J.T. Baker (USA). Helium (99.999%) was used as the carrier gas for GC-MS.

Migration test

This research aimed to study the overall and specific migrations from the PLA/NR films at NR contents ranging from 0 – 25 wt%. The migration test was carried out according to regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food, EN 1186-2:2022 on test methods used for overall migration in vegetable oils, and EN 1186-3:2022 on test methods for overall migration in evaporable simulants.

Overall migration test

The PLA/NR films were cut and immersed in food simulants using a film to food simulant ratio of 6 dm^2/kg at cold or ambient temperatures for short (OM0) and long (OM2) durations, where the contact conditions for OM0 and OM2 are 30 mins and 10 days, respectively, at 40 °C. The food simulants for aqueous and acidic foods are 10% ethanol and 3% acetic acid, respectively. The primary food simulant for oily food which contains free fats at the surface is vegetable oil, and 95% ethanol could also be used as a vegetable oil substitute[7]. The overall migration amount was calculated by Eq. (1) and the test was conducted twice to ensure accuracy.

$$Overall\ migration\ \left(\frac{mg}{dm^2}\right) = \frac{m_s - m_b}{film\ surface\ area} \qquad (1)$$

where m_s and m_b represent the dried weight of remaining residue in the food simulant and in the blank, respectively. For the high-boiling point food simulant (olive oil), the films were sent out to a testing service company due to the unavailability of testing equipment.

Specific migration test

Specific migration from PLA/NR films was evaluated by ED-XRF technique. The migrant solutions from ethanol 95% food simulant were chosen for this test because of their highest OM values. A Shimadzu Energy-Dispersive X-ray Fluorescence (EDX-7000) was used to analyze for inorganic components. The specific migration was conducted twice to ensure accuracy.

Surface morphology test

This test aimed to observe the changes in surface morphology of PLA/NR films before and after being exposed to food simulants at 40 °C for 10 days (OM2). The macroscopic surfaces were observed by using a digital camera, while the microscopic images were obtained by a Field Emission Scanning Electron Microscope (FE-SEM). Before the SEM observation, the specimens were sputtered with gold under vacuum.

Analysis of volatile organic compounds (VOCs)

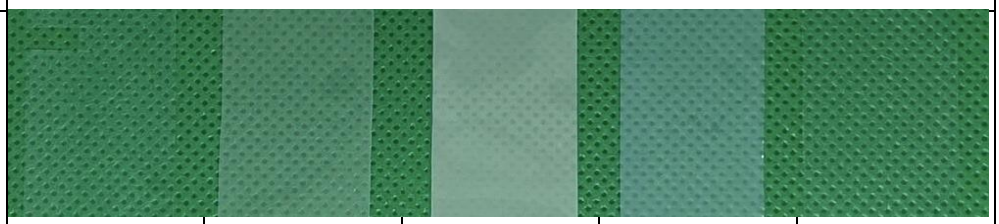
To identify the VOCs emitted from the PLA/NR films, the films were weighed and packed in a headspace vial of a GC-MS. The vial was then incubated with a headspace autosampler at the incubation temperatures (40 °C) for 15 minutes. The VOCs test was conducted twice to ensure accuracy.

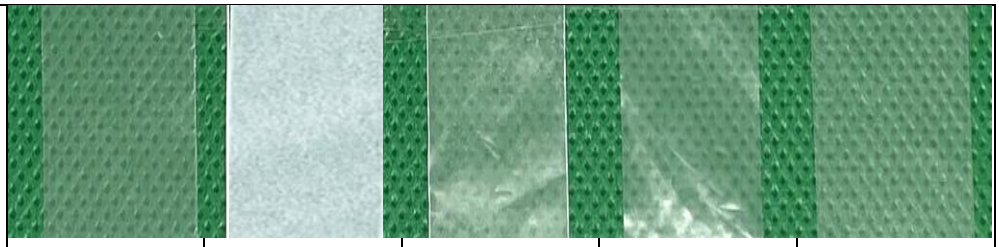
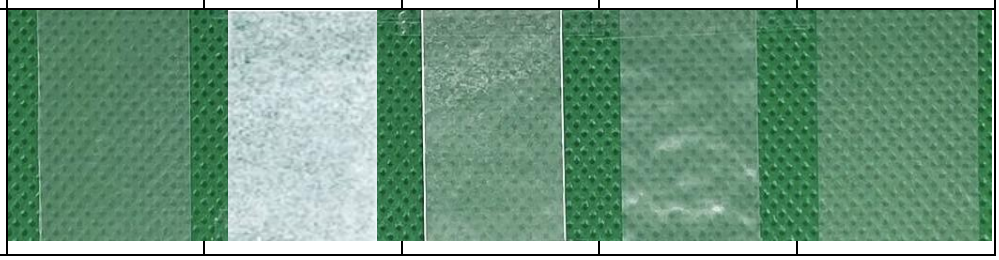
3. Results and Discussion

The changes in surface morphology of PLA/NR films after exposure to food simulants

For a short-term exposure (OM0), all films remained visually unchanged, except for slight wrinkles found in the case of films in 95% ethanol. For the longer exposure time of 10 days (OM2), the visual appearance of the film surfaces is shown in Table 1. As can be seen, the surface of PLA film remained smooth when exposed to all food simulants; however, it turned slightly opaque due to some degree of water and ethanol adsorption. On the other hand, the PLA/NR films turned white in 3% acetic acid solution (Table 1) with a significant change in surface roughness, especially at higher NR contents. In 95% ethanol, the macroscopic view of all films (Table 1) reveals some wrinkles and slight increase in surface roughness without significant rubber agglomeration.

Table 1. The visual appearance of films after exposure to food simulants at OM2 condition

Film samples	Food simulants at OM2 condition				
	Before Test	Acetic Acid 3%	Ethanol 10%	Ethanol 95%	Vegetable oil
Neat PLA					
PLA/10%NR					
PLA/15%NR					

PLA/20%NR	
PLA/25%NR	

Overall migration result

The overall migration from PLA/NR films at NR contents ranging from 0 – 25 wt% was evaluated in four different food simulants: 10% ethanol (v/v), 3% acetic acid (w/v), 95% ethanol (v/v), vegetable oil – under both short-term (OM0) and long-term (OM2) food contact conditions. The overall migration results are shown in Table 2. As can be seen, the overall migrations of films in all types of food simulants at both OM0 and OM2 are in the range of 0 – 4.7 mg/dm^2 (Table 2), which are well below the overall migration limit (OML = 10 mg/dm^2) required by the Regulation (EU) No 10/2011.

Table 2. The overall migration levels of PLA and PLA/NR films under OM2 condition.

Film samples	Overall migration levels (mg/dm^2)			
	3% Acetic acid	10% ethanol	95% ethanol	Vegetable Oil
Neat PLA	0	0.1	1.6	0
PLA/10%NR	0	0.1	2.2	0
PLA/15%NR	0	0.5	3.0	4.7
PLA/20%NR	0	0.6	3.3	0
PLA/25%NR	0	0.9	3.9	0

Specific migration results

The substances that migrated from PLA/NR films at OM2 were identified using XRF and SEM-EDX for inorganic migrants. The XRF results indicated that the migrants from the films with higher NR contents contained higher amounts of Ca element. The source of Ca element was expectedly from $CaCO_3$ used as a non-stick agent for NR. This could be a result of better PLA chain mobility in ethanol (higher swelling) than in water. The higher Ca content detected at higher %NR reveals that the migrants came partly from the migration of $CaCO_3$ from the films.

Analysis of volatile organic compounds (VOCs)

The non-polar VOCs were analyzed by a headspace GC-MS at the incubation temperatures of 40 ^{o}C. It was found that no non-polar VOCs were detected from any films incubated at 40 ^{o}C.

Conclusion

The investigation into chemical migration from PLA/NR packaging films, with NR contents ranging from 0 to 25 wt%, aimed to assess their suitability for food contact and offer insights for product enhancement. The analysis included overall migration (OM), specific migration (SM), and volatile organic compounds (VOCs) emitted from the films. Overall, the OM and SM levels of all PLA/NR films remained well below the maximum limit specified by the EU-regulated standard across all food simulants under both OM0 and OM2. Regardless of low migration levels, the PLA/NR films turned white in aqueous solutions (3% acetic acid and 10% ethanol) potentially posing a perception issue and restricting their application range. Chemical analysis revealed the presence of $CaCO_3$ (used as a nonstick agent for NR). Notably, no VOCs were released from all PLA/NR films at room temperature up to 40 °C. These findings suggested that all PLA/NR films, with NR contents up to 25 wt% exhibit very low overall migration without any toxic substances, thus making them suitable for food packaging across various food types and storage durations at both cold and ambient temperatures.

Authors' contributions

1. N. Chuayrueng: experimental planning and methodology, data analysis, original draft preparation and revision

2. C. Pattamaprom: conceptualization, data analysis, manuscript writing, editing and proof-reading, funding acquisition

All authors have read and agreed to the published version of the manuscript.

Data availability

Supplementary Data are available in supplementary materials.

Funding

This research was funded by Thammasat School of Engineering (TSE), Thammasat University, 2024. In addition, this research was partially supported by Fundamental Fund (FF2567), Thailand Science Research and Innovation (TSRI), Thailand, 2024, and the research unit in polymer rheology and processing, Thammasat University.

Conflicts of Interest

The authors declare no conflict of interest.

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