Fabrication of Natural Rubber Latex Foam Composite Filled with Pineapple-leaf Cellulose Fibres

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Abstract. Pineapple leaf (PL) is a renewable agriculture residue which are abundance in Thailand. In this paper, cellulose powder was extracted from PL. Celluloses are typically used as fillers for rubber reinforced composites due to their properties such as high mechanical properties, low cost, low density, and biodegradability. The aim of this study was to optimize the method to prepare natural rubber latex foam (NRLF) with different cellulose loadings from 0 to 7 phr by using Dunlop method. The different steps for adding celluloses in this study were adding in pre-vulcanization process and in foaming process were studied. The tensile properties, density, compression, and microstructural characterization were studied. Morphological and microstructural performed by using scanning electron microscopy (SEM). It was found that adding cellulose in pre-vulcanization step showed well distribution of cellulose while adding cellulose in foaming process showed the settle of cellulose at the bottom of the foam sample. The tensile strength and elongation at break decreased with increasing of cellulose content whereas modulus increased with increasing of cellulose content.

1. Introduction

Natural rubber latex is a product from Hevea Braziliensis tree. It is 4.3 % market share of Thailand export products. Nowadays, natural rubber is one of the most important raw materials used in the production of elastomers. Elastomers are essential in industries as they can be significantly deformed and still return to their original shape after a release of the applied load. According to achieving this effect, rubber needed to be extensively processed. In the process of vulcanization, the rubber molecules are cross-linked with each other [1]. Moreover, natural rubber can be modified in daily life not only for tires, shoes, or pillows, but also for sponge, rubber glove, and condom with many useful properties such as high elasticity, high tensile strength, and tear resistance [2]. However, natural rubber cannot expose to sunlight or solar which can be harmful to rubber because ultraviolet light (UV) in sunlight can break rubber molecule. Natural rubber then becomes filmy and lose their resilience [3]. Water, rain, and high moisture can cause bacteria and fungus occur in the rubber product surface.

Normally, natural rubber properties can be developed by adding fillers. Fillers can improve performance of materials and reduce cost of material. Reinforcing, semi-reinforcing, and non-reinforcing fillers are three types of fillers. Reinforcing fillers can give better performance in mechanical
properties and abrasion resistance including tensile strength, stiffness, and thermal stability. Moreover, weather resistance and barrier properties are also improved. Celluloses were studied as renewable reinforcing fillers which have high potential for reinforcing with rubber. Celluloses also have a great advantage such as low cost, low density, easy processability, and biodegradability [4]. Agriculture waste can be commonly used as fillers that are abundant on the planet. Cellulose is the most abundant component of plant fibres, along with hemicellulose and lignin. Because of their high tensile strength, elastic modulus, high specific surface area, and lower density.

In this research, celluloses were extracted from pineapple leaves. Moreover, celluloses applied to incorporate with natural rubber latex foam (NRLF). The cross-linking of NRLF were done by pre-vulcanization and post-vulcanization with continuous stirring for 24 hours and using air convection oven respectively. Celluloses were characterization by scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR). Furthermore, the morphological and microstructural of NRLF were performed by using scanning electron microscopy (SEM). The mechanical properties were characterized by compression set, density, and tensile test.

2. Materials and methods

2.1. Materials

PL used in this study was obtained from residues after harvesting pineapple in Prachuap khiri khan province, Thailand. Sodium hydroxide (NaOH) and sodium chlorite (NaClO₂) were purchased from Lab system company limited, Thailand. Natural rubber (60% solids, MST 138 seconds), zinc oxide (ZnO), potassium laurate (K-laurate), potassium hydroxide (KOH), zinc diethyl dithiocarbamate (ZDEC), sulfur, potassium oleate, diphenylguanidine (DPG), and sodiumsilicofluoride (SSF) were purchased from rubber authority of Thailand.

2.2. Extraction of cellulose from pineapple leaves (PL)

Pineapple leaves were milled into powder using a miller machine, and then the powder was sieved (250 μ). Powder (1 gram) was mixed with 4% (w/v) sodium hydroxide aqueous (20 mL) at 80°C for 2 hours by hot plate stirrer. After that, the suspension was filtered using a Büchner set that was attached to a vacuum pump, resulting in sedimentation on the Büchner flask’s filtered paper, and the solid was washed several times with deionized water. The solid was then dried in an oven. This process was repeated until both lignin and hemicellulose has been removed. After that, the treated residue (1 gram) was treated for 1 hour at 90°C with 2.5% (w/v) sodium chlorite solution (20 mL) by hot plate stirrer. After that the suspension was filtered by Büchner set which attached with vacuum pump set so that there was sediment on filtered paper then the solid was washed several times with deionized water. Finally, the solid was dried in an oven. This step was repeated several times.
2.3. Preparation of natural rubber latex foam (NRLF)

The formulations used in this study are shown in Table 1.

| Chemical substances                                      | Content (phr) |
|----------------------------------------------------------|---------------|
| Natural rubber latex with 60% dried rubber content        | 100           |
| 50% Zinc oxide, ZnO                                       | 1             |
| 20% Potassium laurate, K-laurate                          | 0.5           |
| 10% Potassium hydroxide, KOH                              | 0.5           |
| 50% Zinc diethyl dithiocarbamate, ZDEC                    | 1.4           |
| 50% Sulfur                                                | 1.6           |
| 10% Potassium oleate                                      | 1.4           |
| 12.5% SSF                                                 | 2             |
| 33% DPG                                                   | 1             |
| Cellulose                                                 | 0-7           |

* phr = parts per hundred parts of rubber

2.3.1. Method A

Natural rubber latex was stirred in beaker with medium speed for 2 minutes then mixed with ZnO, K-laurate, KOH, ZDEC, and sulfur for 1 minute. After that, it was stirred in closed container for 24 hours to create latex cross-linked with sulfur. It was then beat to evaporate ammonia in Hobart mixer around 5 minutes until volume increased up to three times of initial volume. Then foaming agent were added and filler in the mixture. Then it was poured into mold and allowed to gel 3 minutes. The latex foam was cured in hot air at 110 °C for 1 hours. After that, foam was removed from the mold and washed with distilled water to remove excessive chemicals. Finally, Dried in oven at 55 °C for 24 hours [5].

2.3.2. Method B

Natural rubber latex was stirred in beaker with medium speed for 2 minutes then mixed with ZnO, K-laurate, KOH, ZDEC, sulfur, potassium oleate, and filler for 1 minute. After that, it was stirred in closed container for 24 hours to create latex cross-linked with sulfur. Then it was beat to evaporate ammonia in Hobart mixer around 5 minutes until volume increased up to three times of the initial volume. Then foaming agent (DPG and SSF) was added in the mixer and poured into mold and allowed to gel for 3 minutes. The latex foam was cured in hot air at 110 °C for 1 hours. After that, foam was stripped from mold and washed with distilled water to remove excessive chemicals. Finally, it was dried in an oven at 55 °C for 24 hours [6].

2.4. Characterizations

2.4.1. Morphological analysis of celluloses and NRLF

SEM (FEI, model Quanta 450) was used to observe the surface morphology of PL fibres which are untreated, bleached, and commercial cellulose. Furthermore, SEM was used to observe the cross-sectional area of NRLF samples. Each sample was cracked using liquid nitrogen. The samples were coated with an ultra-thin layer of gold under high vacuum.
2.4.2. Functional group analysis

FT-IR Spectrometer (Perkin-Elmer Spectrum 400) was used to collect data for functional group analysis. Untreated, alkali treated, bleached, and commercial cellulose samples were analyzed. The samples were finely combined with KBr before being compressed into pellets. FTIR spectral analysis was performed within the wavenumber range of 400-4000 cm⁻¹.

2.4.3. Tensile properties

The stress-strain properties of natural rubber latex foam (NRLF) samples were measured by using Instron Universal Testing Machine, model 5965 according to ASTM D412. Five samples were prepared and cut into dumbbell shape by using die cut. The crosshead speed used was 500 mm/min. Tensile strength, elongation at break, and modulus were analyzed.

2.4.4. Compression set

The samples were cut into 50x50x25 mm³ and tested by using Yasuda Foam Rubber Repeated Compression Tester for 72 hours. According to ISO 1856 method B, the samples were compressed to 50±4 % of their original thickness.

2.4.5. Density

The samples were cut into 50x50x40 mm³. Density of foam can be calculated by equation (1) according to ISO 845.

\[
\text{Density (kg/m}^3) = \frac{\text{mass (kg)}}{\text{volume (m}^3)} \times 10^6
\]  

(1)

3. Results and discussion

3.1. Extraction of cellulose from pineapple leaves (PL)

Figure 1 shows morphologies of pineapple leaf fibres before and after chemical treatment compared with commercial cellulose. Figure 1 (a) shows raw pineapple leaf fibres which are bundle and have particulate shapes. Meanwhile, after bleached fibres and commercial cellulose (Figure 1 (b) and (c)) the bundle separates into individual fibres. This may be due to the removal of lignin and hemicellulose [7]. Fibrous shape can make better interaction with the rubber.

Figure 2 shows the FTIR spectra of raw, alkali treated, bleached, and commercial celluloses. The prominent peak at 1734 cm⁻¹ could be attributed to the acetyl and uronic ester groups of hemicelluloses or the ester linkage of carboxylic group of ferulic of lignin and/or hemicelluloses [8,9] and the band near 1254 cm⁻¹ corresponds to the axial asymmetric strain of –C─O─C which is commonly present in ether and phenol groups [10]. Comparing the data shown in FTIR spectra for before and after bleached, it could be noted that the lack of peaks at 1734 cm⁻¹, 1254 cm⁻¹ is due to the significant removal of hemicellulose and mainly lignin by the treatment process. Furthermore, the peak at 1061 cm⁻¹ attributed to the C─O stretching and C─H rock vibrations of the cellulose [11].
3.2. Morphology of natural rubber latex foam (NRLF)

Figure 1. SEM micrographs of cellulose: (a) raw pineapple leaf, (b) after bleaching, and (c) commercial cellulose.

Figure 2. FTIR spectra of (a) Raw pineapple leaf, (b) after alkali treating, (c) after bleaching, and (d) commercial cellulose.

Figure 3. SEM micrographs of cross-sectional surfaces of NRLF composites (method A) at 30x, 100x, 2000x magnification: (a) Neat NRLF, (b) NRLF-1CL, (c) NRLF-3CL, (d) NRLF-5CL, and (e) NRLF-7CL.
Figure 4. SEM micrographs of cross-sectional surfaces of NRLF composites (method B) at 30x, 100x, 2000x magnification: (a) Neat NRLF, (b) NRLF-1CL, (c) NRLF-3CL, (d) NRLF-5CL, and (e) NRLF-7CL.

The SEM micrograph of the cross-sectional area of neat NRLF and NRLF reinforced with varying cellulose loadings are shown in Figure 3 and Figure 4 with different magnifications. The effect of different loading was determined by the pore and the interaction between filler-matrix. The even distribution of pores was observed. Figure 3 (b) to (e) exhibited some fillers in the red circle. The filler filled the pore in the open cell structure demonstrated that the binding between them was not strong. Comparing Figure 3 (b) to (e), the size of pore gradually increased as the filler loading increased. SEM micrographs of Figure 4 were quite similar to those of Figure 3. However, some of fillers prepared by method B filled up in the matrix indicating that it bound better than those from method A.

3.3. Tensile properties

Tensile properties including tensile strength, elongation at break, and modulus were shown in Figure 5 (a) to (c). Tensile strength dropped as filler loading increased attributed to the agglomeration of cellulose in NRLF. This led to low interaction between. Moreover, the fiber surface was not treated by compatibilizer or coupling agents. It was reasonable to state that the strength was not significantly improved. The results of elongation at break determined that it also decreased with increasing filler loading, whereas the results of modulus showed the opposite trend. The incorporation of filler in NRLF tended to increase the rigidity and reduce the elasticity of the foams due to the restriction of the mobility of rubber chains [12,13]. In other studies, similar results have been found. Kudori and Ismail also reported the same tendency in their work [14]. In comparison to method B, Figure 5 (a) to (c) shows that the method A has better tensile strength, elongation at break, and modulus values. This can be explained by the binding between filler and matrix. The results of the SEM images also showed that method B has a stronger filler and matrix binding.

Figure 5. The effect of filler loading on mechanical properties of neat NRLF and NRLF-CL for both method: (a) Tensile strength, (b) Elongation at break, and (c) Modulus.
3.4. Compression set and density

Table 2 shows the effect of different filler loadings on compression set and density. The compression set is a test which measures elastic behavior of NRLF. Generally, the elasticity was decreased with an increase of reinforcing filler loading. Meanwhile, the lower value of compression set showed that the NRLF can maintain better flexibility properties. No significant improvement was obtained by method A. The results of compression set increased then gradually decreased with higher filler loading. However, in method B, compression set increased with higher filler loading due to the NRLF contained aggregated filler. This resulted in the restriction of molecular chain which increased the stiffness of the foam. For method A, the density slightly decreased with more filler loading. The decrease of foam density maybe related with cellular structure. The small dispersed spherical bubbles are generated in liquid matrix may cause a small reduction in density. However, for method B, the density increase with more filler loading maybe caused by an increase in mass of samples [15,16]. It indicates the lower elasticity of NRLF. However, comparing with standard of TIS 2471, method B was more suitable for this standard than method A.

Table 2. Compression set and density of natural rubber latex foam.

| Properties | Method A | Method B |
|------------|----------|----------|
| NRLF       | NRLF -1CL | NRLF -3CL | NRLF -5CL | NRLF -7CL | NRLF       | NRLF -1CL | NRLF -3CL | NRLF -5CL | NRLF -7CL |
| Compression set (%) | 8 | 9 | 7 | 7 | 8 | 4 | 4 | 6 | 7 |
| Density (kg/m³)          | 140.6 | 140.3 | 139.8 | 138.0 | 149.6 | 121.0 | 130.2 | 137.5 | 141.6 | 128.8 |

4. Conclusions

Celluloses were successfully extracted from pineapple leaves which can be confirmed by using FTIR spectra. SEM micrographs showed the fibrous shape of celluloses. NRLF samples corporated with cellulose in pre-vulcanization step showed well distribution of cellulose while adding cellulose in foaming process showed the settle of cellulose to the bottom of the foam sample. The tensile strength and elongation at break decreased with increased of cellulose content, whereas modulus increased with increasing of cellulose content. Moreover, when adding fillers, the density increased when preparing by method A but decrease when preparing by method B. This may be due to cell structure or an increase in mass of celluloses. Compression set increased with higher filler loading due to the restricted of the mobility of rubber chains. However, comparing with standard of TIS 2471, method B was more suitable for this standard than method A.

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