

เส้นใยนาโนเซลลูโลสจากขี้เลื่อยไม้ยางพาราเป็นสารเสริมแรง ในวัสดุเชิงประกอบพอลิแลกติกแอซิด

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บทคัดย่อ

งานวิจัยนี้เป็นการเตรียมเส้นใยนาโนเซลลูโลสดัดแปร (modified NFC) จากขี้เลื่อยไม้ยางพาราซึ่งเป็นเศษไม้จากอุตสาหกรรมเฟอร์นิเจอร์ และถูกใช้เป็นสารตัวเติมเสริมแรงในวัสดุเชิงประกอบพอลิแลกติกแอซิด (PLA) ในการเตรียมเส้นใยนาโนเซลลูโลสดัดแปร ขี้เลื่อยไม้ยางพาราถูกปรับสภาพด้วยสารละลายโซเดียมไฮดรอกไซด์และโซเดียมซัลไฟด์ ฟอกสีด้วยสารละลายโซเดียมคลอไรท์ เซลลูโลสที่ถูกฟอกสีถูกไฮโดรไลซ์ด้วยกรดซัลฟิวริก ความเข้มข้น 64 % โดยน้ำหนัก ที่อุณหภูมิ 45 องศาเซลเซียส เป็นเวลา 3 ชั่วโมง จากนั้นดัดแปรเส้นใยนาโนเซลลูโลส ดัดแปรด้วยเมทิลอะคริเลตเพื่อปรับปรุงอันตรกิริยาระหว่างผิวหน้าของเส้นใยนาโนเซลลูโลสที่มีขี้กับพอลิแลกติกแอซิดที่ไม่มีขี้ด้วยวิธีกราฟท์โคพอลิเมอร์เชน เทคนิค Fourier-transform infrared spectroscopy (FT-IR) ถูกใช้เพื่อพิสูจน์ การเปลี่ยนแปลงของหมู่ฟังก์ชันบนเส้นใยนาโนเซลลูโลสหลังการดัดแปรผิวหน้า วัสดุเชิงประกอบถูกเตรียมด้วยการหลอมผสมที่อุณหภูมิ 180 องศาเซลเซียส ผลของเส้นใยนาโนเซลลูโลสหลังการดัดแปรต่อสมบัติของพอลิแลกติกแอซิดถูกวิเคราะห์เปรียบเทียบกับเส้นใยนาโนเซลลูโลสที่ไม่ถูกดัดแปร (unmodified NFC) โดยวิเคราะห์สมบัติการวางกัน สมบัติทางความร้อน และสมบัติเชิงกลของวัสดุเชิงประกอบเทียบกับพอลิแลกติกแอซิด ผลการทดลองแสดงให้เห็นว่าค่าอัตราการซึมผ่านไอน้ำ (WVTR) ของฟิล์มพอลิแลกติกแอซิดที่เติมเส้นใยนาโนเซลลูโลสที่ถูกดัดแปร มีค่าต่ำที่สุด สำหรับ อุณหภูมิเปลี่ยนสถานะคล้ายแก้ว (T_g) ของพอลิแลกติกแอซิดที่เติมเส้นใยนาโนเซลลูโลสที่ถูกดัดแปร มีค่าสูงกว่าพอลิแลกติกแอซิดที่เติมเส้นใยนาโนเซลลูโลสที่ไม่ถูกดัดแปร นอกจากนี้ผลการวิเคราะห์สมบัติเชิงกลพลวัต (DMA) แสดงว่าเส้นใยนาโนเซลลูโลสที่ถูกดัดแปรเพิ่มมอดูลัสสัมผัสให้แก่พอลิแลกติกแอซิด แต่เพิ่มอัตราการคืบของพอลิแลกติกแอซิดเมื่อเทียบกับเส้นใยนาโนเซลลูโลสที่ไม่ถูกดัดแปร

คำสำคัญ: เส้นใยนาโนเซลลูโลส, ขี้เลื่อยไม้ยางพารา, พอลิแลกติกแอซิด, การดัดแปรผิวหน้า

Nanofibrillar cellulose from Para Rubber Wood Sawdust as reinforcement in Polylactic Acid Composites

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ABSTRACT

This work prepared the modified nanofibrillar cellulose (modified NFC) from Para rubber wood sawdust, namely the wood residues from furniture industries and used it as a reinforcing filler in polylactic acid (PLA) composite. To prepare the modified NFC, Para rubber wood sawdust was pretreated with NaOH and Na_2S and bleached with NaClO_2 . The bleached cellulose was then hydrolyzed with 64%wt of H_2SO_4 at 45 °C for 3 hours. The obtained NFC was modified with methyl acrylate (MA) to improve interfacial interaction between NFC and hydrophobic PLA by grafting method. Fourier-transform infrared spectroscopy (FT-IR) was employed to investigate the changes of the functional groups on NFC after modification. The composites were prepared by melt blending at 180 °C. The effects of the modified NFC on the properties of PLA composites were investigated compared to the unmodified NFC. Barrier, thermal and mechanical properties of the composites and neat PLA were measured. The results showed that the water vapor transmission rate (WVTR) value of the PLA/modified NFC composite film was lowest. The glass transition temperature (T_g) of the PLA/modified NFC composite was higher than that of the PLA/unmodified NFC composite. Moreover, the dynamic mechanical analysis (DMA) showed that the modified NFC improved the storage modulus, but increased creep rate of PLA matrix as compared to the unmodified NFC.

Keywords: nanofibrillar cellulose, Para rubber wood sawdust, polylactic acid, surface modification

Introduction

In the few decades, nanocellulose has attracted interest for environmentally friendly materials due to its renewable nature, low weight and excellent mechanical properties. It has been widely used in various applications such as nanopaper, films, foams and medical devices [1, 2]. Moreover, nanocellulose can be used as reinforcing agent in polymer nanocomposites [3, 4]. According to Sung et al. [5], the barrier and mechanical properties of polylactic acid (PLA) were improved by addition of 3% cellulose nanocrystals (CNCs). The results showed that the barrier and mechanical properties of nanocomposite films were improved. Since cellulose is an organic component of the cell wall of plants occurring in wood, cotton, hemp and agricultural residues [6]. Para rubber tree (*Hevea brasiliensis*) is one of the most economically important tree in Thailand because the milky latex extracted from the tree is the primary source of natural rubber, and the wood was harvested for furniture making. Kasikranan [7] reported that the Para rubber raw material production in 2007 reached a value of 3.24 million tons and then it should reach a figure of 4.16 million tons in 2020. As a result, there are many tons of wood sawdust from wood processing plant in Thailand. This work is interested in using Para rubber wood sawdust as a cellulosic material to create value added product, namely nanocellulose.

Polylactic acid (PLA) was produced from renewable resources, for instance, corn, potato, cane sugar, and rice [8]. It was used in medical and packaging applications, but the main limitations of PLA were poor thermal, mechanical, and gas barrier properties. The addition of renewable and biodegradable fillers like nanocellulose could improve the performance of PLA [9]. However, according to the hydrophilic nature of cellulose, nanocellulose was not easy to uniformly disperse in hydrophobic PLA matrix. Surface modification of nanocellulose was needed to improve their interfacial compatibility [10]. There are many methods for modification of nanocellulose including acetylation, silylation, application of coupling agents and grafting [11]. Pracella et al [12] reported that the PLA containing cellulose nanocrystal (CNC) functionalized with glycidyl methacrylate (GMA) by grafting improved the phase distribution of CNC and tensile properties, compared to the PLA/unmodified CNC nanocomposite.

In this work, nanofibrillar cellulose (NFC), one type of nanocellulose, was prepared from Para rubber wood sawdust using H_2SO_4 acid hydrolysis and modified using radical grafting of methyl acrylate (MA). Melt blending method was used for the composites preparation. The effects of surface modification on water vapor permeability, mechanical and thermal properties of composites were studied.

Materials and Methods

1. Materials

Para rubber wood sawdust was collected from wood processing plant in Rayong, Thailand. Methyl acrylate (MA) and ammonium cerium (IV) nitrate (CAN) were purchased from Sigma-Aldrich. Sodium hydroxide, sodium sulfide, sodium chlorite, acetic acid, sulfuric acid, nitric acid, acetone and chloroform were analytical grade. Cellulose dialysis tubing with a molecular cutoff of 12,000-14,000 daltons was purchased from Carolina. Polylactic acid (IngeoTM 3251D) was purchased from Nature Friend Co., Ltd.

2. Extraction of nanocellulose

Nanocellulose was prepared using the method modified from Li et al. [13]. The 30 g of Para rubber wood sawdust was soaked in hot distilled water for 2 h. The ratio of sawdust to solution is 1:20. The sawdust was pretreated with 1 w/v% NaOH solution at 80 °C for 2 h, followed by washing with hot distilled water. The sawdust was then treated by 1 w/v% NaOH solution with the addition of 1 w/v% Na₂S at 80 °C for 1.5 h to remove lignin and hemicellulose. After removal of lignin and hemicellulose, the sawdust was washed with hot distilled water and bleached by 0.7 v/v% sodium chlorite with an acetate buffer at 80 °C for 1.5 h to remove the lignin residues. The bleached fibers were washed repeatedly by distilled water and air-dried. The obtained cellulose was then hydrolyzed with 64 w/w% of H₂SO₄ at 45 °C for 3 h. The bleached fibers to acid solution ratio are 1:20. When the reaction was end, 10-fold cold distilled water was added to the mixture. The resulting mixture was centrifuged at 4,500 rpm for 10 minutes. The precipitate was re-suspended in distilled water and followed by a centrifugation for six centrifugation cycles to remove the excess sulfuric acid. The precipitate was then dialyzed against distilled water until neutrality was attained. The final suspension was homogenized at 10,000 rpm for 30 minutes to get the nanofibrillar cellulose (NFC) suspension with NFC content of 0.2 ± 0.5 w%.

3. Modification of nanocellulose

NFC was modified by grafting with methyl acrylate (MA). The method used was modified from Pracella et al. [12] and Littunen et al. [14]. The 0.2 ± 0.5 w% of NFC suspension was adjusted to pH 1 with diluted HNO₃, stirred and heated to 35 °C for 15 minutes. The initiator, ammonium cerium (IV) nitrate (CAN), 2 mmol/L was added and stirred for 15 minutes. Methyl acrylate (MA) was then added for 40 mmol/g of dry NFC, and the mixture was stirred for 1 h. The mixture was centrifuged, and the precipitate was washed with distilled water. The precipitate was washed with acetone to separate the homopolymer from graft copolymer, respectively as follows [15],

$$\text{Grafting percentage} = \frac{W_1 - W_0}{W_1} \times 100 \quad (1)$$

$$\text{Grafting efficiency} = \frac{(W_1 - W_0)}{(W_1 - W_0 + W_2)} \times 100 \quad (2)$$

where W_1 , W_0 , and W_2 are the weights of the cellulose graft copolymer, the original cellulose, and the homopolymer, respectively.

4. Composites preparation

0.2 ± 0.5 w% of NFC suspension was solvent exchanged to acetone by centrifugation, then mixed with PLA powder prepared by dissolving in chloroform and air-drying. The mixture later indicated as masterbatch (20 w/w% of NFC or modified NFC) were dried in oven at 80°C for 12 h. The masterbatches were added into PLA, PLA to NFC ratio (or PLA to modified NFC ratio) of 99:1, and melt blended using internal mixer at 180°C for 6 minutes with 60 rpm of rotor speed. The composites were compression molded to films at 180°C for 8 minutes.

5. Characterization

Chemical structures of original sawdust, bleached cellulose fiber, NFC and modified NFC were characterized using a FTIR spectrometer (Nicolet 6700, Thermo Scientific, Canada). The samples were dried at 80 °C for 12 h to completely remove the moisture. The testing samples were obtained after grinding with KBr. FTIR spectra of samples were obtained over range of 4000-400 cm⁻¹.

Dynamic light scattering (DLS) technique (Zetasizer Nano ZS, Malvern, USA) was used to measure the average particle size (X_{DLS}) and polydispersity index (PI) of NFC suspension. The size distribution of the NFC in aqueous suspension (0.2 ± 0.5 w%) was calculated three times at 25°C using plastic disposable cuvettes.

In order to investigate the crystallinity of original sawdust, bleached cellulose fiber and NFC, the samples was measured by step scanning on a X-ray diffractometer (D8 Discover, Bruker, Germany) over the angular range $2\theta = 5^\circ$ - 70° with a scanning rate of 5 °C/min. The crystallinity index (CI) of each sample was calculated according to the Segal's method [16].

$$CI (\%) = \frac{I_{(200)} - I_{(am)}}{I_{(200)}} \times 100 \quad (3)$$

where $I_{(200)}$ is the adsorption peak intensity of the (200) reflection (at $2\theta = 22^\circ$). $I_{(am)}$ is the minimum adsorption intensity between (110) and (200) peaks (at $2\theta = 16^\circ$).

Thermal stabilities of neat PLA, PLA/unmodified NFC and PLA/modified NFC composites were recorded on a thermogravimetric analyzer (TGA/DSC 3+, Mettler Toledo,

Switzerland). The composite samples were weight for about 6 mg and then heated from 30°C to 600 °C at the rate of 10°C/min.

Dynamic mechanical analysis with tension fixture mode (DMA1, Metter Toledo, Switzerland) was used to investigate viscoelastic properties of the composites. Two types of tests including DMA with dynamic temperature scan and creep test were performed. For DMA testing, the temperature heating scan rate were used from 30°C to 120°C with heating rate of 3°C/min and frequency of 1 Hz. The creep test was measured at 25°C with a constant force at 4 N.

The WVTR measurements were performed by using the sample film with thickness of 0.13 ± 0.03 mm to seal a homemade container containing 5 g of silica gel, and then kept at 30°C 50 %RH for 24 h. The decrease in weight was measured and the WVTR values were calculated using the following equation [17].

$$\text{WVTR} = \frac{\text{sample weight change}}{\text{area} \times \text{time}} \text{ (g/m}^2\text{/d)} \quad (4)$$

Results

1. Preparation of NFC

The NFC sample appeared to be translucent and homogeneous suspension. The process yield based on the amount of consumed Para rubber wood sawdust and produced NFC was 18.6 ± 1.3 %. The average particle size (X_{DLS}) and polydispersity index (PI) of NFC was 59.2 nm and 3.3, respectively.

From the FTIR spectra as shown in Figure 1, the rubber sawdust showed peaks at 1730 cm^{-1} and 1246 cm^{-1} which attributed to the C=O stretching and C-O stretching vibration of hemicellulose, respectively. The peaks at 1506 cm^{-1} stood for the aromatic C=C stretching of aromatic ring in lignin [18]. These peaks disappeared in the spectrum of bleached fiber and NFC due to the removal of hemicellulose and lignin from rubber wood sawdust during the chemical extraction. The band at 1640 cm^{-1} was assigned to the absorbed water. The most significant absorption band at 897 cm^{-1} associated with the C-O-C glycosidic linkages between glucose units in cellulose increased on bleached fiber and NFC, respectively.

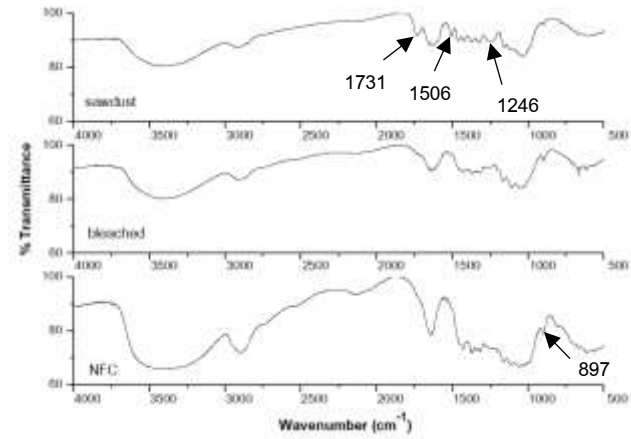


Figure 1 FTIR spectra of original sawdust, bleached cellulose fiber and NFC.

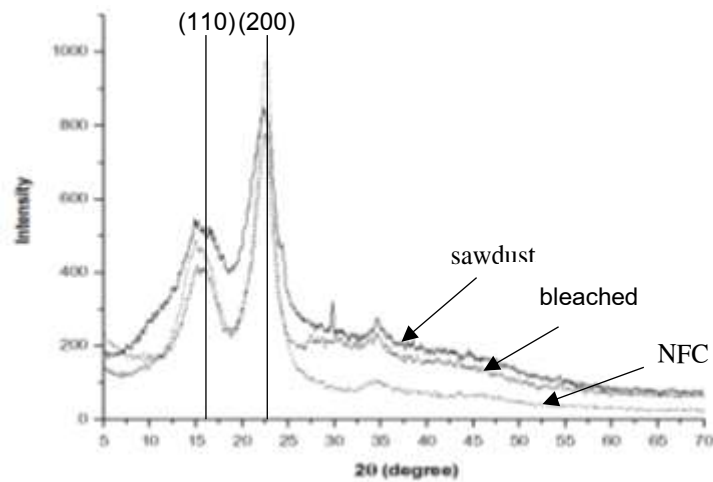


Figure 2 XRD curves of original sawdust, bleached cellulose fiber and NFC.

Figure 2 showed the XRD curves of original sawdust, bleached cellulose fiber and NFC. The peak positions of all samples were at $2\theta = 22^\circ$ and at $2\theta = 16^\circ$, corresponding to the cellulose I structure [17]. The crystallinity was increased from 52.9 % for rubber sawdust, to 70.2 % for bleached fiber, and to 72.5 % for NFC. The increase of crystallinity found in each process could be explained by the removal of hemicellulose and lignin, which acted as amorphous regions in cellulose [18, 19].

2. Modification of NFC

The successful modification of MA on NFC was confirmed by FTIR as shown in Figure 3. The spectrum of modified NFC showed characteristic peaks of carbonyl group of MA at 1733 cm^{-1} and 1180 cm^{-1} , indicating to C=O and C-O vibration, respectively [11, 13]. The grafting yield and grafting efficiency were founded as $13.7 \pm 4.1\%$ and $88.1 \pm 1.4\%$, respectively.

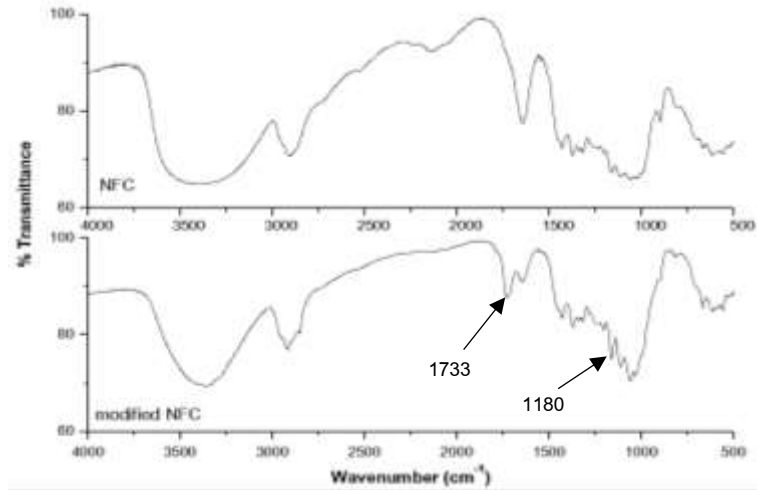


Figure 3 FTIR spectra of unmodified and modified of NFC using methyl acrylate as a monomer.

3. Properties of composites

Figure 4 showed the TGA and DTG curves of PLA, PLA/unmodified NFC, and PLA/modified NFC analyzed at the heating rate of $10^{\circ}\text{C}/\text{min}$. The neat PLA started to thermally decompose at 346°C while the initial decomposition temperature of NFC was 184°C . This was because the sulfate groups accelerated the beginning of weight loss and increased char yield [18]. A significant decrease in initial decomposition temperature was observed for the PLA/modified NFC (106°C) due to the methyl acrylate groups on NFC surface as discussed in the FTIR results.

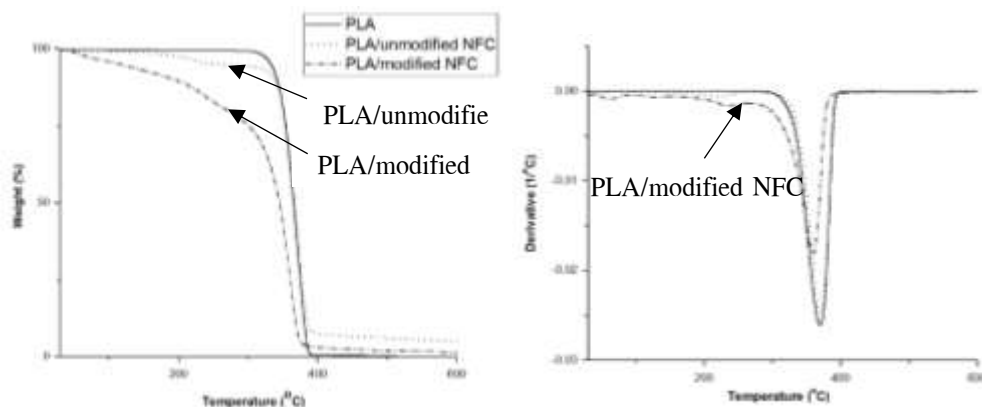


Figure 4 TGA and DTG of PLA, PLA/unmodified NFC and PLA/modified NFC composites.

From Figure 5, The DMA results showed that the modified NFC improved the storage modulus of PLA matrix from 2273 MPa to 2601 MPa. The glass transition temperature (T_g) of the PLA/modified NFC composite from $\tan \delta$ peak was higher than that of the PLA/unmodified NFC composite. This was due to the improved interfacial interaction between NFC and PLA. The results from creep test in Figure 6 showed that the PLA containing either unmodified NFC or modified NFC had higher creep rate than the neat PLA. Besides, it was found that the MA modified NFC slight demoted the creep resistance of the composites, as compared to the unmodified NFC.

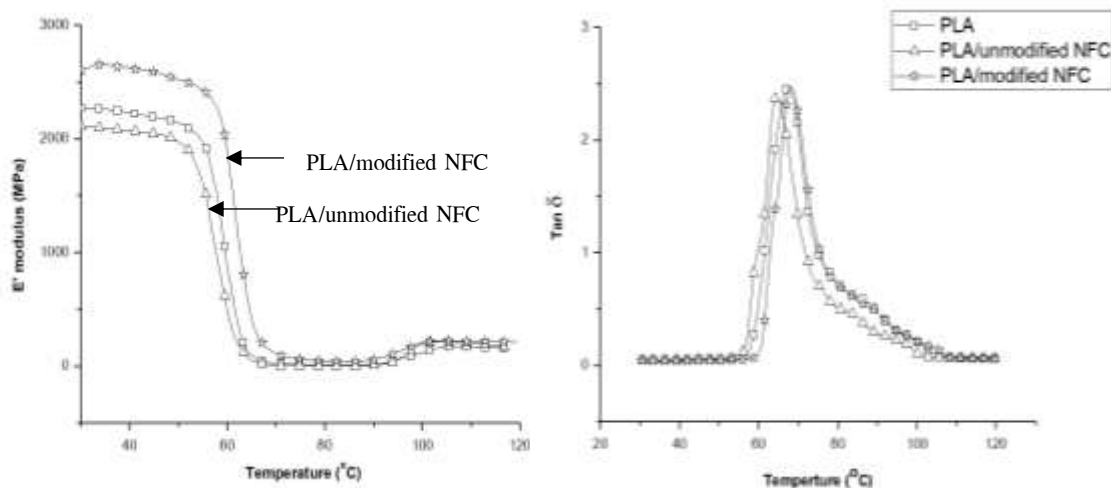


Figure 5 Storage modulus and $\tan \delta$ as a function of temperature of PLA, PLA/unmodified NFC and PLA/modified NFC composites.

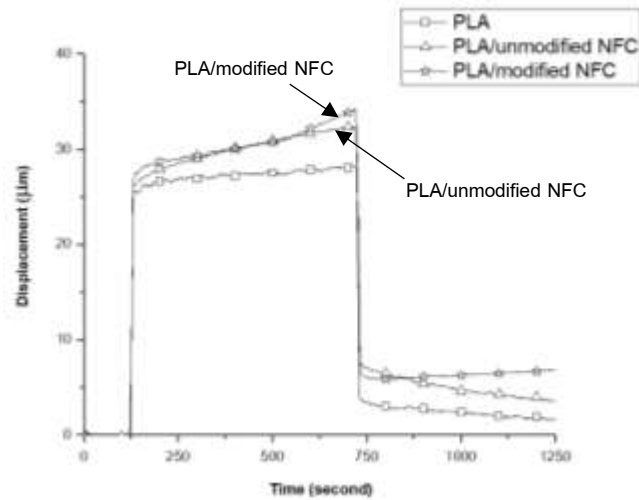


Figure 6 Creep test curves of PLA, PLA/unmodified NFC and PLA/modified NFC composites.

According to Figure 7, the water vapor transmission rate (WVTR) values of composite films with the thickness of 0.13 ± 0.03 mm were measured at 30 °C, 50 %RH. The results showed that the WVTR value of PLA film was 11.3 ± 0.3 $\text{g/m}^2/\text{d}$. The lowest WVTR observed from the PLA/modified NFC was 10.3 ± 0.3 $\text{g/m}^2/\text{d}$, while the unmodified NFC had no effect on the WVTR of PLA composites (11.0 ± 0.1 $\text{g/m}^2/\text{d}$).

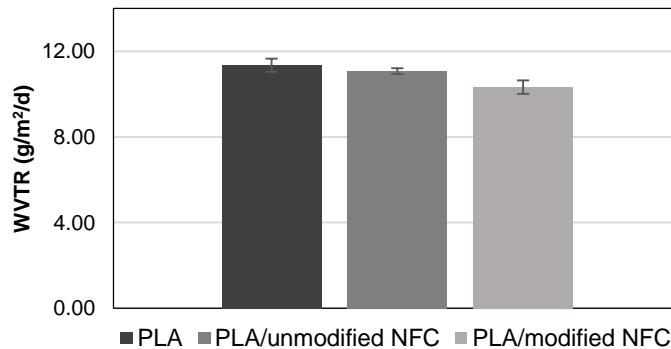


Figure 7 WVTR testing of PLA of PLA, PLA/unmodified NFC and PLA/modified NFC composites.

Conclusion and Discussion

In this work, the NFC was successfully prepared from Para rubber wood sawdust by acid hydrolysis. The crystallinity of NFC was increased from 52.9 % for rubber sawdust to 72.5 % because of the removal of lignin and hemicellulose. Modification of NFC with MA monomer was confirmed by FTIR spectroscopy. The result showed the characteristic peaks of carbonyl group of MA. The grafting percentage (%GP) and grafting efficiency (%GE) were 13.7 ± 4.1 % and 88.1 ± 1.4 %, respectively. The thermal stability of PLA composites containing NFC and modified NFC decreased because of sulfate groups and methyl acrylate groups on NFC surface. The modified NFC improved the storage modulus, but increased creep rate of PLA matrix as compared to the unmodified NFC. The WVTR value of the PLA composite was improved by the addition of MA modified NFC. This result can be explained by a lower hydrophilicity of the modified NFC. Moreover, the hydrophobic modification of NFC provided a good compatibility [17] of NFC and PLA. Thus the nanofibers could uniformly disperse in the matrix, leading to the enhancement of barrier properties. Based on the results, the modified NFC, extracted from Para rubber wood sawdust, was promising for use as a reinforcing filler in PLA matrix.

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References

1. Mohammad, T. I., Mohammad, M. A., Politecnico D. T., Alessia, P., Alessio, M., and Marina, Z. 2014. Preparation of Nanocellulose: A Review. *AATCC Journal of Research*. 1(5): 17-23.
2. Tiffany, A., Amit, R., Yifeng, C., Yuval, N., Eldho, A., Tal, B. S., Shaul, L., and Oded, S. 2016. Nanocellulose, a Tiny Fiber with Huge Applications. *Current Opinion in Biotechnology*. 39: 76-88.
3. Lee, K. Y., Aitomäki, Y., Berglund, L. A., Oksman, K., and Bismarck, A. 2014. On the Use of Nanocellulose as Reinforcement in Polymer Matrix Composites. *Composites Science and Technology*. 105: 15-27.
4. Spinella, S., Re, G. L., Liu, B., Dorgan, J., Habibi, Y., Leclere, P., Raquez, J. M., Dubois, P., and Gross, R. A. 2015. Polylactide/cellulose Nanocrystal Nanocomposites: Efficient Routes for Nanofiber Modification and Effects of Nanofiber Chemistry on PLA Reinforcement. *Polymer*. 65: 9-17.

5. Sung, S. H., Chang, Y., and Han, J. 2017. Development of Poly(lactic Acid) Nanocomposite Films Reinforced With cellulose Nanocrystals Derived from Coffee Silverskin. *Carbohydrate Polymers*. 169: 495-503.
6. Khalil, H. P. S. A., Bhat, A. H., and Ireana Yusra, A. F. 2012. Green Composites from Sustainable Cellulose Nanofibrils: A Review. *Carbohydrate Polymers*. 87(2): 963-979.
7. Kasikranan, S. 2010. Para Rubber (*Hevea brasiliensis*) Cultivation, Production and Trading of Para Rubber Raw Materials in the Greater Mekong Sub-region (GMS). *RMTTO Journal*. 4(2): 1-9. (in Thai)
8. Frone, A. N., Berlioz, S., Chailan, J. F., and Panaitescu, D.M. 2013. Morphology and Thermal Properties of PLA–cellulose Nanofibers Composites. *Carbohydrate Polymers*. 91: 377-384.
9. Fortunati, E., Peltzer, M., Armentano, I., Torre, L., JimÉnez, A., and Kenny, J. M. 2012. Effects of Modified Cellulose Nanocrystals on the Barrier and Migration Properties of PLA Nano-biocomposites. *Carbohydrate Polymers*. 90: 948-956.
10. Abdulkhani, A., Hosseinzadeh, J., Ashori, A., and Dadashi, S. 2014. Preparation and Characterization of Modified Cellulose Nanofiber Reinforced Poly(lactic Acid) Nanocomposite. *Polymer Testing*. 35: 73-79.
11. Eyley, S., and Thielemans, W. 2014. Surface Modification of Cellulose Nanocrystals. *Nanoscale*. 6: 7764-7779.
12. Pracella, M., Haque, M.U. and Pugli, D. 2014. Morphology and Properties Tuning of PLA/cellulose Nanocrystals Bionanocomposites by Means of Reactive Functionalization and Blending with PVAc. *Polymer*. 55: 3720-3728.
13. Li, R., Fei, J., Cai, Y., Li, Y., Feng, J., and Yao, J. 2009. Cellulose Whiskers Extracted from Mulberry: A Novel Biomass Production. *Carbohydrate Polymers*. 76: 94-99.
14. Littunen, K., Hippi, U., Johansson, L. S., Osterberg, M., Tammelin, T., Laine, J. and Seppälä, J. 2011. Free Radical Graft Copolymerization of Nanofibrillated Cellulose with Acrylic Monomers. *Carbohydrate Polymers*. 84: 1039-1047.
15. Gurdag, G., and Sarmad, S. 2013. Cellulose Graft Copolymers: Synthesis, Properties, and Applications. *Polysaccharide Based Graft Copolymers*. p. 15-57.
16. Segal, L., Creely, J. J., Martin, A. E., and Conrad, C. M. 1959. An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer. *Textile Research Journal*. 29(10): 786-794.

17. Song, Z., Xiao, H., and Zhao, Y. 2014. Hydrophobic-modified Nano-cellulose Fiber/PLA Biodegradable Composites for Lowering Water Vapor Transmission Rate (WVTR) of Paper. *Carbohydrate Polymers*. 111: 442-448.
18. Tian, C., Yi, J., Wu, Y., Wu, Q., Qing, Y., and Wang, L. 2016. Preparation of Highly Charged Cellulose Nanofibrils using High-pressure Homogenization Coupled with Strong Acid Hydrolysis Pretreatments. *Carbohydrate Polymers*. 136: 485-492.
19. Mandal, A., and Chakrabarty, D. 2011. Isolation of Nanocellulose from Waste Sugarcane Bagasse (SCB) and Its Characterization. *Carbohydrate Polymers*. 86: 1291-1299.

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