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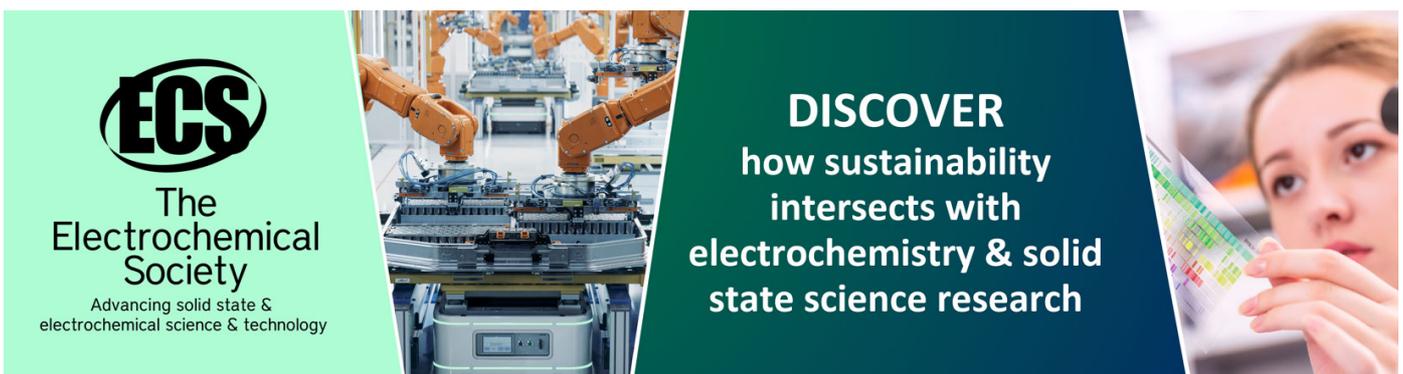
Improvement of thermal and mechanical properties of composite based on polylactic acid and microfibrillated cellulose through chemical modification

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Improvement of thermal and mechanical properties of composite based on polylactic acid and microfibrillated cellulose through chemical modification

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Abstract. Polylactic acid (PLA) is the most representative sustainable and bio-based polymer environmentally friendly that has a great potential to replace petroleum-based plastics. However, brittleness, low heat resistance, and slow crystallization limit the wide application of PLA. One of strategies to improve PLA properties is by reinforcing with microfibrillated cellulose (MFC). Unfortunately, the hydrophilic properties of MFC make it difficult to attain good dispersion in a hydrophobic PLA matrix. Therefore, modification of MFC was needed to increase its compatibility with PLA in the composite formation. In this experiment, MFC was modified with partial acetylation (degree of substitution: 1) and further grafted with lactide monomers through ring-opening polymerization using Sn(Oct)₂ catalyst. The result of acetylation and grafting were verified by infrared spectra. Composites were prepared by mixing PLA (molecular weight of 200,000) and the modified MFC at 9:1 ratio through organic solvent method. Followed by 8 min-kneading and hot pressing at 180°C, the resulted composites were evaluated for their mechanical and thermal properties. Thermal characterization carried out using differential scanning calorimetry measurements showed that the presence of modified MFC increased the temperature of glass transition and accelerated the crystallization of PLA. Mechanical properties measurement showed that the presence of modified MFC enhanced the elongation at break (1.1 to 1.8%), tensile strength (14.9 to 25.7 MPa), and modulus of elasticity (1.7 to 2.1 GPa). These results demonstrated that the modified MFC could extend the application of PLA in industry.

1. Introduction

In recent years, the concepts of green chemistry, green materials, and industrial ecology in the field of polymers have been developed. This concept aims to answer the environment problem and depletion of fossil oil resources. Polylactic acid (PLA) is one of the environmental-friendly polymers, which is versatile, made of renewable materials, energy and the production cost are low that can compete with other synthetic polymers. PLA is potential as an alternative substitution of petroleum-based polymers in the industrialized world. By its nature, PLA has good mechanical properties that are easily used in the manufacture of technical fiber and films, extrusion and thermoforming, and injection molding. However, it has some weakness including fragile, low stability and heat resistance,



and the slow rate of crystallization. The weakness limits its industrial application [1]. Several studies reported that addition of microfibrillated cellulose (MFC) improved PLA properties [2][3].

In the application, MFC is used as filler in the PLA matrix. Its small size (10^{-9} - 10^{-6} m) makes this nanofiber more effective as reinforcing compared to other fibers [4] and it is potential as a reinforcing material in the automotive industry, buildings, computers, and other products. Thus the formation of MFC-reinforced composite can give them the advantage in terms of the physical, thermal, and mechanical [5]. However, MFC has hydrophilic properties that inhibits its dispersion in the PLA matrix, forming a hydrophobic aggregation of the MFC and irreversible agglomeration due to strong hydrogen bonds. This makes composite formed with a low thermal stability [1]. Several researches were conducted to improve MFC properties either by exploring more sources of MFC [6] or by converting MFC to Nanofiber Cellulose (NFC) [7]. Therefore, some chemical modifications should be carried out with the aim of improving compatibility.

Partial acetylation in bacterial cellulose with a range of degree of substitution (DS) 0.04-2.77 had been reported by Kim *et al.*, (2002) [8]. The result showed that acetylation occurs on the surface of bacterial cellulose and does not damage the fiber morphology. Ifuku *et al.*, (2007) [9] had modified the bacterial surface nanocellulose acetylated fibers with various DS. Acetylation is able to improve various properties of fibers, effectively reduce the hygroscopicity of the bacterial nanocellulose, and enhance compatibility with other hydrophobic materials such as PLA matrix.

Another approach in reducing the hydrophilicity of MFC was reported by Goffin *et al.*, (2011) [1]. The surface of nanocellulose was grafted with polyester matrix using ring-opening polymerization of L-lactide, followed by mixing PLA to form a composite. Toluene was used as a solvent and $\text{Sn}(\text{Oct})_2$ as a catalyst in the ring opening polymerization. Thermal property characterization of the composite indicated that such modification improves compatibility and also increases the strength of the composite. In preparing the PLA-MFC composite, Iwatake *et al.*, (2010) [10] used 2 methods, namely direct mixing and blending in organic solvent. Based on the mechanical properties of the products, it was suggested that mixing in organic solvent gave a better composite than that prepared through direct mixing.

This experiment aimed to improve thermal and mechanical properties of composite based on PLA and MFC through chemical modification to obtain a better homogeneity between the PLA and MFC. Partial acetylation allowed hydrophilic hydroxy groups at MFC structure partially substituted by acetyl groups that are hydrophobic, so that MFC could be compatible with hydrophobic materials such as PLA matrix. The acetylation product hereinafter was called MFC-acetate. The next process was grafting the MFC-acetate by employing lactide monomer. Lactide monomer was expected to grow at

the backbone structure of MFC. The final step was preparing some composite which was expected to have some thermal and mechanical properties improved.

2. Materials and Methods

2.1 Materials

The materials used were MFC (Daicel Chemistry, Japan), lactide monomer (Sigma-Aldrich), Sn(Oct)₂ (Sigma-Aldrich) as polymerization catalyst, and PLA H-400 (Toyota).

2.2 Acetylation of MFC

Approximately 10 g wet MFC was squeezed using chamois until water seeps out. The sample was placed in a flask and 50 mL ethanol was added while stirring for 30 min. The suspension was then filtered using a suction means. The procedure was repeated by replacing ethanol with acetone and glacial acetic acid. After removing the free water, the sample was added dropwise an acid catalyst (CH₃COOH:H₂SO₄ 95-97% (v/v) = 100:1) as much as 12 mL and allowed to stand for 1 min. Furthermore, some more acetic anhydride was slowly added (15 mL). The suspension was stirred by glass rod until thickened, allowed to stand for 90 min (started when acetic anhydride was added). The acetylation process was stopped by adding mixture of 3 mL of glacial acetic acid:distilled water (2:1) and allowed to stand for 30 min (stirring at medium speed in order to mix evenly). Samples that had been acetylated MFC was then dispersed into 500 mL of distilled water by vigorous stirring. The product was then vacuum-filtered by Büchner funnel and washed with NaHCO₃ 1 N until there was no more CO₂ bubbling out. The fiber was washed with distilled water until neutral (pH 6.5-7) and vacuum-filtered until water no longer dripping. Samples that had been acetylated were stored in tightly lid glass jar.

2.3 Grafting on MFC-acetate by Lactide Monomer through Ring Opening Polymerization

Samples of MFC-acetate that had been obtained previously (DS ± 1) were immersed in acetone and dried using toluene by centrifugation techniques. The samples were suspended in toluene in a three-necked reaction flask, stirred, and purged with nitrogen. The reaction flask was immersed in a water bath and heated to 80 °C. Then, 1 g of L-lactide monomer (in hot toluene) was added to the reaction flask containing the MFC-acetate suspension. Sn(Oct)₂ (2% of the monomer weight) was added through a sterilized needle to catalyzed the reaction. Polymerization was carried out for over 24 h, and stopped by adding a few drops of dilute HCl solution (0.1 M). Graft copolymerization products were obtained by precipitation in cold methanol and filtered.

2.4 Composite Preparation

The double modified MFC (10% weight of the intended composite) was suspended in methanol for 15 min and filtered. The ethanol was replaced by acetone and dichloromethane successively. Each inclusion process was repeated 3 times. In a separate beaker, PLA (90% of the intended composite weight) was dissolved in dichloromethane using a homogenizer to obtain a well-dispersed suspension. The suspension formed was stirred and the modified MFC was gradually added to the suspension at room temperature and kept stirring for 1 h. The blend of PLA/modified MFC in dichloromethane was spread out on a basin and evaporated in a fume hood at room temperature for 12 h followed by vacuum drying at 50 °C for 8 h. The composite layer was dried, weighed, and cut up ($\pm 1 \text{ cm}^2$). In the next process, the composite was kneaded using laboplastomil at 160 °C, at 40 rpm speed for 8 min. Finally, the composite was molded into thin sheets using hot pressed at 180 °C for 14 min (preheating 6 min, pressing 3 min under 400 Pa, and cooling 5 min).

3. Results and Discussion

3.1 Microfibrillated Cellulose

MFC is cellulose which has been acid-hydrolysed [1] and mechanically processed in homogenized high pressure and a small aggregate [13]. According to Chakraborty *et al.*,(2006) [14], MFC has reached 0.1-1 μm fiber diameter and minimum length of 5-50 μm . Based on morphological analysis using SEM (Figure 1) with a magnification of 1000 \times the fiber diameter was varied (111.7-157.9 nm), while the length is difficult to measure because each fiber is tangled in webs.

Cellulose microfibril consists of crystalline and amorphous regions in interspersed proportion depending on cellulose source obtainment. In addition, this compound has a regular structure in the form of a linear polymer repeat unit due to β -D-glucopyranose are linked to each other through β (1-4) bonds. Two hydroxy groups in position C2 and C3 (secondary) and that in C6 (primary) create intra- and intermolecular hydrogen bonds. Therefore, the cellulose fibers have high tensile strength and is insoluble in most solvents. Cellulose, and therefore, the MFC also shows strong hydrophilic character, as proven its moisture content as high as 90%. This strong hydrophilic character of MFC inhibits dispersion in the PLA matrix.

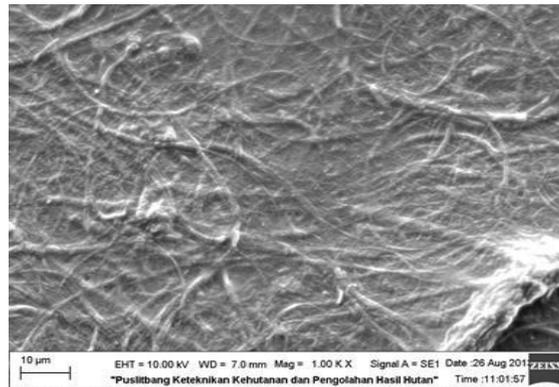


Figure 1. Morphology of MFC with 1000× magnification.

3.2 Modified MFC

Acetylation was meant to chemically modified MFC in order to alter certain properties based on their structure. In this study, the hydroxy groups on MFC was not completely acetylated, just sufficiently to render its compatibility with the hydrophobic PLA. Partial acetylation reaction in MFC-acetate can be evidenced by the degree of substitution (DS), as determined by titration techniques.

The DS of MFC-acetate was approximately 1. However, Ifuku *et al.*, (2007) [9] reported DS of 0.2 to 0.6 did not alter cellulose crystallinity region significantly, the extent of hydrogen bonds between cellulose fibers only slightly reduced. In this experiment, DS <1 was not obtained, presumably due to the use of sulfuric acid as a catalyst in acetylation causing structural deformation of the MFC. This was evidenced by the dissolution of the MFC when mixed with acetic anhydride and sulfuric acid. The deformation caused the acetylation of cellulose structure did not only occur on the surface of cellulose but all layers of cellulose fibers.

Analysis using FTIR spectrophotometer on neat-MFC, MFC-acetate, and MFC-acetic-lactic grafted (MFC-acetate-g-La) is shown in Figure 2 and Table 1. There is a typical absorption of cellulose at wavenumber 3236 cm^{-1} and wavenumber 1053 cm^{-1} belongs to -CO stretching on the cellulose ring. Furthermore, the intensity of the -OH absorption peak decreases and typical sharp absorption peak appears that belong to cellulose acetate, indicating -CO stretch (1759 cm^{-1}) and acetyl -CO bend (1234 cm^{-1}) [15]. The spectrum shows that the decrease in absorption intensity is due to partially substituted of the hydroxy groups by acetyl groups.

The second step of modification was graft copolymerization with lactide monomer by ring opening polymerization techniques. The graft copolymer can produce copolymer that is similar to the main chain and the grafted monomer, so that through graft copolymerization, the polymer properties can be modified in accordance with the purpose and utilization.

Table 1. Infrared spectra of neat MFC and modified MFC

MFC		MFC-asetat		MFC-asetat-g-La	
Wave number(cm^{-1})	Fungsional Group	Wave number(cm^{-1})	Fungsional Group	Wave number(cm^{-1})	Fungsional Group
3236	O-H stretching	3630	O-H stretching	3527	O-H stretching
2890	C-Hstretching	2947	C-Hstretching	2960	C-Hstretcing
1650	O-Hbend	1759	C=Ostretching	1752	C=Ostretching
1390	C-Hbend	1375	C-Hbend	1375	C-Hbend
1053	C-Ostretching	1234	C-Oacetate	1235	C-Oacetate
		1042	C-Ostretching	1047	C-Ostretching
		608	C-Hbend	604	C-Hbend

Covalent bonds between the main chain of the polymer grafts and ensure the permanence. Ring-opening polymerization technique is a good technique for polymerization using monomers such as cyclic lactone and lactide. Result of grafting on MFC-acetate is presented in Figure 2.

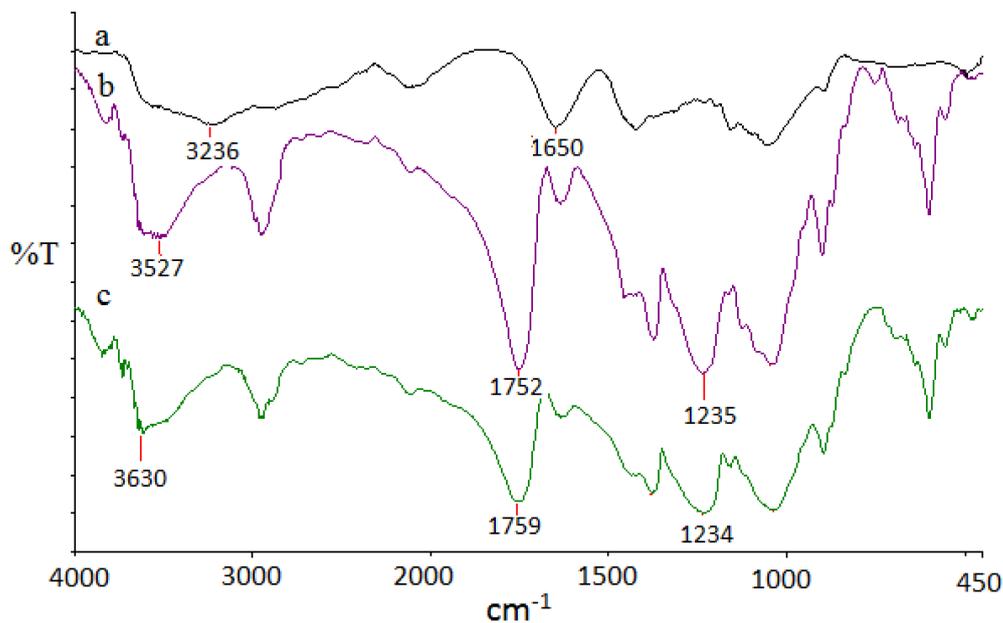
**Figure 2.** Spectrum of neat MFC (a), MFC-acetate (b) and MFC-acetate-g-La (c)

Figure 2 shows the absorption peaks are relatively similar to the spectrum of MFC-acetate, namely wavenumber 3527 cm^{-1} that belongs to $-\text{OH}$ group, 1752 cm^{-1} belongs to $-\text{CO}$ group, and 1235 cm^{-1} belongs to $-\text{CO}$ acetyl group [15]. There is a trend of declining peak intensity of the free $-\text{OH}$ and increasing peak intensity of $-\text{CO}$ acetyl group, showing that the lactide has been grafted on the MFC-acetate backbone.

3.3 Analysis of Thermal Properties

Thermal properties of composites in this study were characterized using DSC instrument applying heat microscopy (scanning of low temperature to high temperature) and produced a thermogram curve. The thermogram curve displays the glass transition temperature (T_g), crystallization temperature (cold state) (T_c), and melting temperature (T_m) of the material being tested. Figure 3 displays the thermogram curve of neat-PLA, PLA composite/MFC, and composite PLA / MFC-acetate-g-La, respectively. Based on the analysis of the thermogram third curve (Table 2) shows that the T_g of PLA / MFC-acetate-g-LA (54.38°C) higher than the T_g of neat PLA (52.81°C) and PLA/MFC (49.33°C). The shift of temperature indicated that the PLA reinforced with modified MFC can increase T_g . Increasing T_g fairly well because when the composite was subjected to heat, the rubber phase change to a higher temperature so that it was more heat-resistant than neat-PLA.

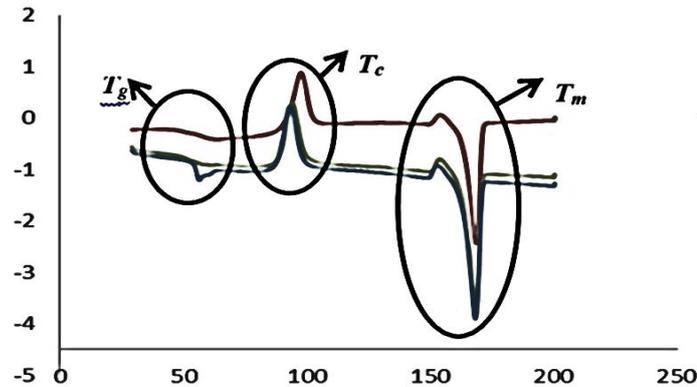
The increase was caused by when the PLA receives thermal energy, the polymer molecules is activated and induces vibrational and rotational motion. The presence of acetylated and lactylated MFC as filler reduced the flexibility of the molecular structure of PLA and inhibited the molecules vibration and rotation so that the high energy is required to achieve a T_g . In addition, Braun *et al.* [14] reported that the grafted-MFC formed percolation network on the filler particles that providing increase to T_g . Otherwise, the PLA/MFC (not modified) actually showed a reduction in the T_g . The phenomenon occur due to the unmodified MFC having incompatibility with PLA to form a weak interaction between the filler and the matrix, so that causing the T_g decline.

Based on crystallinity data, T_c PLA/MFC-acetate-g-La (93.20°C) and PLA/MFC (94.01°C) is lower than T_c of neat- PLA (97.60°C) (Table 1). This shows that the decrease in T_c PLA reinforced with MFC was able to crystallize faster than neat- PLA. This is due to MFC action as a nucleating agent [12]. However, T_c of PLA/MFC-acetate-g-La is higher than PLA/MFC. The difference proves that the modifications to the MFC is able to improve the compatibility between the PLA. Thus, the effectiveness of the MFC as a nucleating agent can be further increased when dispersed evenly in the PLA matrix.

However, the melting data was not influenced by MFC as reinforcement in the PLA matrix. Based on data from T_m (Table 2), there was no significant decrease between T_m of PLA/MFC (168.29°C) and T_m PLA/MFC-acetate-g-La (168.31°C) when compared with neat PLA T_m (168.35°C). In the application, the T_m peak effect, fast or slow the process of getting molten form. The lower the temperature, it is better because it is faster to get a discharge considering PLA products have a narrow temperature range up degraded.

Table 2. Analysis of measurement results with DSC

Sampel	T _g (°C)	T _c (°C)	T _m (°C)
Neat-PLA	52.81	97.60	168.35
PLA/MFC	49.33	94.01	168.29
PLA/MFC-acetate-g-La	54.38	93.20	168.31

**Figure 3.** Thermogram of DSC where the upper line is neat PLA, the middle line is PLA/MFC, and the lower line is PLA/MFC-acetate-g-La

3.4 Analysis of Mechanical Properties

Reinforcing effect of MFC modified on the PLA matrix demonstrated through testing of mechanical properties: the elongation at break, tensile strength, and modulus of elasticity. Results of the analysis on the mechanical properties of neat-PLA, PLA/MFC, and PLA/MFC-acetate-g-La are shown in Table 3. It's known that the elongation break of modified or not modified sample showed no significant change, which is neat- PLA (1.18%), PLA/MFC (1.42%), and PLA/MFC-acetate-g-La (1.77%). However, it appeared that the presence of MFC as filler provides enhanced mechanical properties, although not real. This phenomenon occurs due to the interaction between MFC and PLA composite extend the point of deformation.

MFC reinforcement effect seen in rigidity and tensile strength of the resulting composites. All these facts proved that the MFC was able to increase the strength of the PLA. This increase was due to percolation network; cellulose fibers act as filler to strengthen the structure and were able to keep the stiffness matrix of PLA [3]. In addition, fillers restrict the movement of the molecular chain of the amorphous PLA [15].

Table 3. The result of mechanical strength test using UTM

Sample	Elongation at break (%)	Tensile strength (MPa)	Mod. Elasticity (GPa)
PLA	1.1±0.2	14.9±0.3	1.7±0.2
PLA/MFC	1.3±0.3	17.7±0.3	2.0±0.2
PLA/MFC-Acetate-g-La	1.8±0.3	25.7±2.2	2.1±0.1

However, dissolution of MFC on acetylation process was expected to affect strength of produced MFC-acetate and certainly have an impact on the composite strength of PLA/MFC-acetate-g-La. When MFC was soluble, it was suspected for structure deformation that makes hydrogen bonding between cellulose chains broken to form a space in the crystalline chain so that when the MFC-soluble is dispersed in water, the MFC that has not formed a tight crystalline structure as originally tough to prove it needs to be analyzed morphological crystalline using x-ray diffraction (XRD). The phenomenon was thought to be the cause of rigidity values PLA/MFC-acetate-g-La does not vary much with PLA/MFC.

PLA/MFC-acetate-g-La had a rigidity and a higher tensile strength compared with PLA/MFC. This difference proves that the MFC which had been modified (acetylated and lactylated) had a better compatibility with the PLA matrix than unmodified MFC. It is caused when a composite accept load (energy), then the energy will first be accepted by the matrix and then be transferred to the fibers as filler through the interface field. Therefore, the ability of the interface in the field of energy transfer from the matrix to the filler play an important role on the mechanical strength of a composite.

The good compatibility will form a large surface area of between matrix and filler so that the composite is able to transfer energy better. The presence of grafting in this study to increase the strength of a composite due to the formation of covalent bonds between the MFC and the grafted polymer chains [1] and will increase compatibility due to increased adhesion between the two bonds. In addition, the partial acetylation support grafting reaction in improving the strength of the composite produced. According to Braun *et al.*, (2013) [16], limiting the degree of grafting on the MFC through partial acetylation process successfully form a network thereby increasing the rigidity and strength of the composite.

4. Conclusions

The reinforcement of modified MFC improved the thermal and mechanical properties of PLA composites. Thermal characterization carried out using differential scanning calorimetry

measurements revealed that the addition of modified MFC increased the temperature of glass transition and accelerated the crystallization of PLA. Furthermore, mechanical properties measurement showed that the addition of modified MFC enhanced the elongation at break from 1.1 to 1.8%, tensile strength from 14.9 to 25.7 MPa, and modulus of elasticity from 1.7 to 2.1 GPa. Thus the MFC modified (acetylated) can improve the properties of PLA composites.

Acknowledgement

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