Manufacture of Nanocomposites Based On Microfibrillated Cellulose and Polylactic Acid

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Abstract

This study evaluates the manufacturing process of microfibrillated cellulose (MFC) reinforced PLA nanocomposites using a semi-crystalline grade of polylactic acid (PLA). The objective of this study was to obtain uniform dispersion of MFC in a PLA compound of semi-crystalline grade of PLA. The nanocomposites were prepared by mixing MFC and PLA in an organic solvent followed by drying, kneading and hot pressing into sheets. XRD was performed to evaluate crystallinity of the composites and DMA was used to evaluate mechanical properties (rigidity). We found that dichloromethane is effective to dissolve semi-crystalline grade PLA, a high-performance disperser can obtain well-dispersed suspension of composites, kneading process can homogenize the compound, and immersing in liquid N2 after hot pressingis effective to obtain amorphous state samples.

Keywords: Polylactic acid, microfibrillated cellulose, nanocomposites, thermo-mechanical properties.

1. Introduction

Plastics have replaced many conventional materials in various applications because of the ease of processing, high productivity, and substantial cost reduction that are possible with polymers [1]. Since most of the plastics currently in use are petroleum-based polymers, petroleum depletion and a growing environmental awareness throughout the world have motivated many scientists to develop plastics from bio-based polymers. There are many polymers produced from biological resources such as starch, polyhydroxy butyrate (PHB) and polylactic acid (PLA).

Among bio-based plastics, polylactic acid (PLA) has a great potential to replace petroleum-based plastics because of its high mechanical properties, which are comparable to polystyrene (PP). PLA is a versatile polymer made from renewable agricultural raw materials such as corn starch that are fermented to lactic acid, which is commonly polymerized by the ring-opening polymerization of the cyclic lactide dimer [2]. In addition, PLA can be processed in a way similar to that used with polypropylene. However, low rigidity at high temperature and a slow crystallization speed limit the wider application of PLA [2-3].

The use of lignocellulosic materials as reinforcement of PLA has been studied with the goal of obtaining fully bio-based composites [2-5]. The main advantages of lignocellulosics compared to inorganic fillers are their renewability, low cost, and low density [3]. The thermo-mechanical properties of PLA have been investigated using plant and pulp fibers as reinforcement [4-9]. They observed, even though the rigidity of PLA increased significantly with an increase of plant fiber content, but the strength decreased.

Recently, microfibrillated cellulose (MFC), which consists of pulp that is mechanically fibrillated into nanofibers forming a web-like network, has received significant research attention. Zimmerman et al. [10] reported that mechanical properties of MFC-reinforced hydroxypropyl cellulose (HPC) prepared by film casting has three times higher tensile modulus and five times higher tensile strength compared with the matrix without reinforcement. Nakagaito and Yano [11] demonstrated that nanocomposites produced by compression molding of MFC sheets impregnated with phenol formaldehyde (PF) resin have high bending

strength and modulus comparable to magnesium alloy. In other compelling applications, nanocomposite materials based on MFC and melamine formaldehyde (MF) resulted in high mechanical damping, showing their potential to be used as loudspeaker membranes [12], and adding MFC to polyurethane (PU) drastically improved heat resistance [13].

In a recent study, Iwatake et al. [14] developed a technique to attain uniform dispersion of MFC in amorphous PLA matrix using the so-called solvent method (premixing of fibers and matrix in an organic solvent medium) followed by kneading, and they demonstrated that the tensile modulus of amorphous PLA improves without a reduction of yield strain at a fiber content of up to 10 wt%. The MFC reinforcement increased the tensile strength of neat PLA by 25%. However, the poor rigidity of amorphous PLA matrix at high temperatures restricts its application, particularly as a structural material.

Considering that the crystallinity of PLA influences the thermal and mechanical properties of PLA composites [15,16], to improve the storage modulus, we subsequently studied MFC-reinforced PLA composites using a semi-crystalline grade PLA as the matrix. Thus, in this paper, we studied the appropriate production procedure to attain uniform dispersion of MFC in a PLA compound of semi-crystalline grade of PLA.

2. Materials and Methods

2.1. Materials

Matrix: PLA trade name LACEA H-100, supplied by Mitsui Chemicals, Inc., Japan. The density is 1.26 g/cm^3, glass transition temperature (T_g) is 58 °C, and melting point (T_m) is 164°C. The melt flow rate (MFR) is 8 g/10 min (190°C, 2.16 kg). Table 2.1 shows physical and mechanical properties of PLA LACEA H-100 and H-280 for comparison, provided by manufacture.

Reinforcement: Microfibrillated cellulose trade name Celish KY-100G, was supplied by Daicel Chemical Industries, Ltd., Japan. MFC is a cellulose morphology produced by mechanical fibrillation of wood pulp fibers and consists of a web of interconnected fibrils and microfibrils greatly expanded in surface area. This product consists of 10 wt% fiber content slurry. PLA and MFC are illustrated in Fig. 1.

Table 2.1 Physical and mechanical properties of PLA LACEA H-100 and H-280

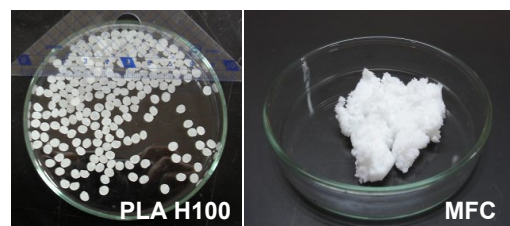| Physical and Mechanical Properties	LACEA H-100	LACEA H-280
MFR	8	2.5
Melting Point (°C)	164	no data
Tensile strength (MPa)	73	68
Elongation (%)	5	6
Flexural strength (MPa)	104	99
Flexural modulus (MPa)	3320	3240
Izod impact strength (j/m)	29	no data
Rockwell hardness	120	107
Vicat softening point (°C)	58	55
Heat distorsion temperature (°C)	54	52

Fig 1 PLA LACEA H-100 and MFC

2.2. Solubility test

The solubility test was carried out to find a suitable solvent for dissolving the semi-crystalline grade of PLA (LACEA-H100). First, 1g of PLA H100 was dissolved in 50 ml of various solvents; ethanol, acetone, hexane, dichloromethane, tetrahydrofuran and chloroform. The PLA was immersed in the solvent at room temperature for 1 hour without stirring (Fig.3).

2.3. Solvent exchange

To replace water in the MFC slurry, 1 wt% MFC suspension in acetone was prepared. The MFC was thoroughly dispersed in the solvent by stirring, and then followed by centrifugation to remove the liquid phase. The process was repeated 3 times in order to completely replace water by acetone. Next, the acetone was replaced by dichloromethane following the same method, repeating the process 2 times. This process to successively replace water by acetone and dichloromethane is hereafter referred as "solvent exchange" method.

2.4. *Dispersing treatment*

The suspension of MFC in dichloromethane solvent was treated by a high-performance disperser (Ultra-Turrax T25 Basic, IKA-Werke GmbH & Co. KG, Germany) for 2 minutes at 3000 rpm to obtain a well dispersed suspension Fig. 2.

Fig 2 Ultra-Turrax T25 Basic

Table 2.2 The compound formulation of PLA/MFC composites

Percentage of MFC (%)	MFC (g)	PLA (g)	Total (g)
0	0.0	60.0	60.0
3	1.8	58.2	60.0
5	3.0	57.0	60.0
10	6.0	54.0	60.0
20	12.0	48.0	60.0

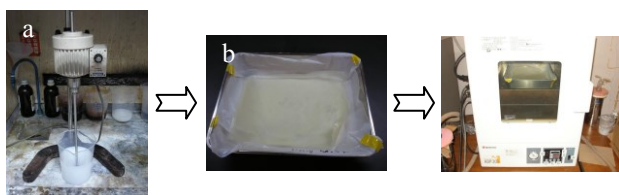## 2.5. *Solvent evaporation*

Fig 3. Solvent casting processes: a) mixing, b) drying at room temperature, and c) vacuum drying at 50°C

MFC suspension (1 wt% MFC in dichloromethane) was stirred in a beaker. When the MFC was thoroughly dispersed in the solvent, PLA was gradually added to the suspension. After complete dissolution of PLA, the stirring was kept for 2 hours. The MFC-dichloromethane-PLA mixture was spread in trays and the solvent was evaporated in a fume hood at room temperature for 12 hours followed by vacuum-drying at 50 °C for 8 hours Fig. 3. The mixture formulation of PLA/MFC composites is presented in Table 2.2.

2.6. *Kneading treatment*

The mixture from which the solvent had been removed was kneaded using a twin rotary roller mixer (Labo Plastomill, Toyo Seiki Seisaku-sho, Ltd., Japan) at 160 °C, 40 rpm for 15 min to obtain a homogeneous compound.

Fig. 4. Kneader

2.7. *Hot pressing and cooling system*

The compound was hot pressed into films at 180°C in three steps: 5 min with no pressure, 5 min at 0.5 MPa, and 5 min at 1 MPa. After hot pressing, the melted samples were treated by three different methods:

Method 1: the samples were immediately immersed in liquid N_2 to obtain fully amorphous samples which hereafter we call the liquid N_2 cooling system.

Method 2: the samples were cooled using water flow through the hot press plates which hereafter we call the water cooling system (WCS). Cooling speed is around 12°C/min from 160°C to 60°C.

Method 3: the samples were kept in the hot press at 100 °C for 60 min to obtain highly crystalline samples.

Fig. 5. Hot press

The effect of cooling methods after hot pressing was studied using X-ray diffraction (XRD) and dynamic mechanical analysis (DMA) measurements.

2.8. *X-ray diffraction*

The diffraction patterns were obtained from the radiation generated by the copper target of a Rigaku UltraX 18HF (Rigaku Corporation, Japan) set at 20 kV and 100 mA with the detector placed on a goniometer scanning from 5° to 45°.

2.9. *Dynamic mechanical analysis*

The dynamic mechanical analysis was performed on a Rheovibron, DDV-25FP (Orientec A&D, Co. Ltd., Japan), with a chuck distance of 21 mm and a frequency of 1 Hz. The test specimens of 4 mm in width, 40 mm in length, and 0.5 mm in thickness were cooled to -10°C with liquid N_2, maintained at this temperature for 10 min, and then heated to 150°C at a heating rate of 2°C/min.

Fig. 6. Solubility test just after PLA was added to the solvents a) ethanol, b) acetone, c) hexane, d) dichloromethane, e) tetrahydrofuran, and f) chloroform

Fig. 7. Solubility test after 60 minutes: a) ethanol, b) acetone, c) hexane, d) dichloromethane, e) tetrahydrofuran, and f) chloroform

3. Results and Discussion

3.1. *Solubility test*

Solubility test of PLA in various solvents was conducted to find a suitable organic solvent for dissolving PLA. At the beginning of testing (0 min) PLA sank in all solvents except for dichloromethane and chloroform, where PLA floated Fig. 6. After 60 minutes without stirring at room temperature (around 20°C), PLA almost completely dissolved in

dichloromethane and chloroform but showed no visible changes in other solvents (ethanol, acetone, hexane and tetrahydrofuran). Fig. 7. shows the solubility test result after 60 min with PLA immersed in various solvents.

Methylene chloride or dichloromethane (DCM) is the chemical compound with the formula CH_2Cl_2. It is a colorless, volatile liquid with a moderately sweet aroma. It is widely used as a solvent, the general view being that it is one of the less harmful of the chlorocarbons, and it is miscible with most organic solvents. Since dichloromethane has lower boiling point and is less harmful compared to chloroform, we decided to use dichloromethane as solvent for dissolving PLA.

3.2. *Solvent exchange*

The solvent exchange method consists in replacing water by acetone and dichloromethane in succession, as detailed in Material and Methods section. Fig. 8 shows the results of MFC dispersion directly in dichloromethane. Fig. 9 shows the results of MFC dispersion in dichloromethane using acetone as intermediate solvent, here referred as solvent exchange.
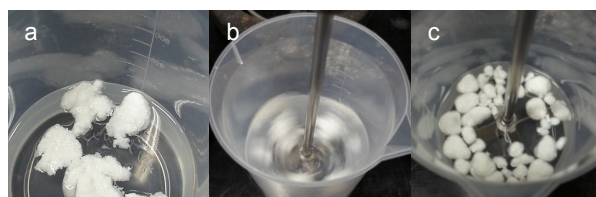

Fig 8. MFC directly dispersed in dichloromethane; a) before stirring, b) during stirring, and c) after stirring
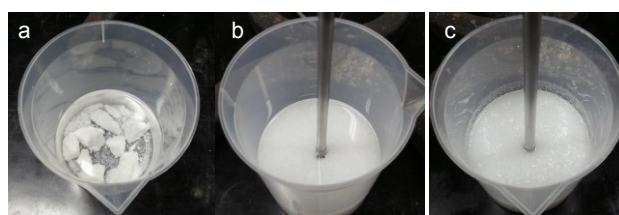

Fig. 9. MFC gradually dispersed in acetone followed by dichloromethane; a) MFC in acetone before stirring, b) MFC in acetone during stirring, and c) MFC in dichloromethane during stirring

The dispersion did not occur when MFC was directly diluted in dichloromethane. We obtained a good

suspension of MFC in dichloromethane after MFC was gradually dispersed in acetone and then the acetone was replaced by dichloromethane Fig. 9 .

3.3. *Evaluation of dispersion*

During the mixing of MFC in dichloromethane by the solvent exchange method, surface interaction between fibers may occur due to hydrogen bonding resulting in some agglomeration. In order to avoid these agglomerations, a high-performance disperser (Ultra-Turrax T25 Basic) was used to disperse MFC in the solvent. Fig. 10 shows a MFC suspension before and after dispersing treatment, with a significant change in the dispersion. We could obtain well-dispersed MFC in dichloromethane after the treatment.
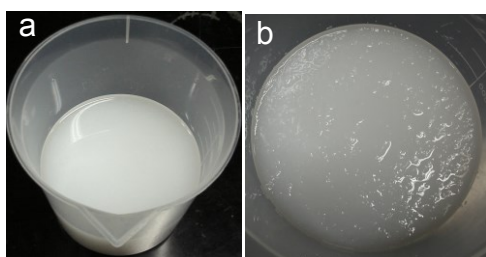

Fig 10. MFC suspension in dichloromethane; a) before and b) after dispersing treatment

3.4. *Solvent evaporation*

The density of MFC is higher than that of PLA, so MFC sinks in the PLA solution during evaporation of the solvent. To avoid such a sink, the MFC-dichloromethane-PLA mixture was spread in large trays during the evaporation.

The glass transition temperature (Tg) of PLA LACEA H-100 is 58 °C. To avoid crystallization during the drying process, the solvent of the MFC/PLA mixture was completely evaporated under vacuum condition at 50 °C (below Tg). When crystallization occurs during the drying process, a higher temperature is needed to melt the mixture resulting in degradation of PLA during the subsequent kneading process.

3.5. *Kneading*

Kneading was conducted to obtain homogeneous PLA/MFC compounds. Fig. 11 shows the composites that were produced with and without the kneading step. The effect of kneading results in more transparent sheet films due to better dispersion of fibers in the composites.
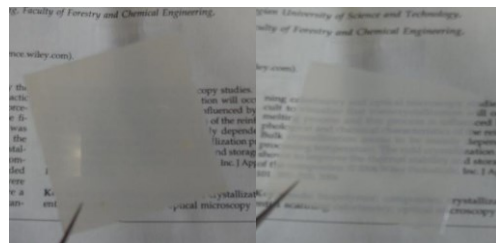

Fig. 11. PLA/MFC sheets: a) without kneading and b) with kneading

3.6. *Hot pressing and cooling system evaluation*

Dynamic mechanical analysis (DMA) and X-ray diffraction (XRD) measurements were performed to evaluate the effect of cooling methods after hot pressing.

XRD data

Fig. 12 and Fig. 13 show the XRD patterns of PLA and MFC/PLA composite using liquid N_2 cooling system and water cooling system, respectively. As a comparison, the XRD patterns of crystallized PLA and MFC/PLA composites are presented in Fig. 14.
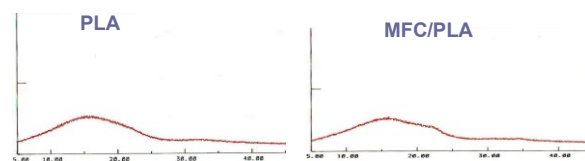

Fig. 12. X-ray diffraction of neat PLA and MFC/PLA composite with liquid N2 cooling system

Based on the X-ray data, the diffraction patterns of both neat PLA and MFC/PLA composite using liquid N_2 cooling system have no peak of crystalline region. In this case, the liquid N_2 cooling system was effective to obtain fully amorphous samples. Meanwhile the diffraction patterns of PLA and MFC/PLA composite using water cooling system show peaks of crystalline region for MFC/PLA composite but there is no peak of

crystalline region for neat PLA, showing that water cooling system with cooling speed around 12 °C/min to reduce the temperature from 160 to 60 °C is not fast enough to avoid crystallization in order to obtain fully amorphous MFC/PLA composites. Furthermore, the diffraction patterns of crystallized PLA and MFC/PLA composite show peaks of crystalline region for both neat PLA and MFC/PLA composite, indicating that both samples are crystalline.
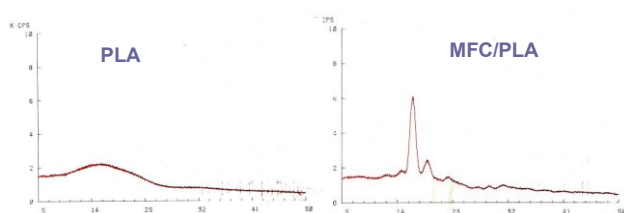

Fig. 13. X-ray diffraction of neat PLA and MFC/PLA composite using water cooling system
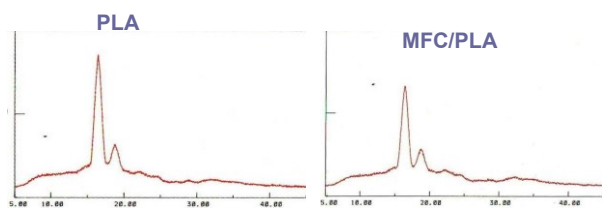

Fig. 14. X-ray diffraction of crystallized neat PLA and MFC/PLA composite

DMA data

Fig. 15 shows the temperature dependence of storage modulus of neat PLA and composites with different treatments after hot pressing. Based on the DMA curves for neat PLA (Fig. 15a), the curves of PLA cooled by using liquid N_2 and water cooling system have almost the same storage modulus at a temperature of 80°C (above Tg), indicating that both samples are amorphous. If their storage modulus were different, the possibility is that one of them has higher degree of crystallinity. The curve of crystallized PLA is shown as comparison.

In the curves of composites (Fig. 15b), at a temperature of 80 °C (above Tg), the curve of the sample cooled by using water cooling system has storage modulus higher than the one using liquid N_2 system, indicating that water cooling system is not effective to obtain amorphous condition.

Based on the X-ray data and DMA curves, we can say that the liquid N_2 cooling system is effective to obtain fully amorphous samples for both neat PLA and MFC/PLA composites.
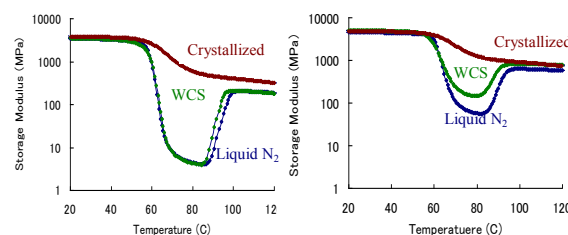
Figure 2.1   Temperature dependence of storage modulus of a) neat PLA and b) PLA/MFC 10 wt% with different treatments after hot pressing (immersed in liquid N_2, cooled by water cooling system, and crystallized at 100°C for 60 min)

Fig. 15. Temperature dependence of storage modulus of a) neat PLA and b) PLA/MFC 10 wt% with different treatments after hot pressing (immersed in liquid N_2, cooled by water cooling system, and crystallized at 100°C for 60 min)

4. Conclusion

In this study, the manufacturing process of MFC reinforced PLA nanocomposites using a semi-crystalline grade of PLA have been established. The nanocomposites were prepared by mixing MFC and PLA in an organic solvent followed by drying, kneading and hot pressing into sheets. XRD was performed to evaluate crystallinity of the composites and DMA was used to evaluate mechanical properties (rigidity). We found that dichloromethane is effective to dissolve semi-crystalline grade PLA, a high-performance disperser can obtain well-dispersed suspension of composites, kneading process can homogenize the compound, and immersing in liquid N_2 after hot pressingis effective to obtain amorphous state samples. Furthermore, this procedure will be adopted for the production of samples in the following studies.

5. Acknowledgement

6. References

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