Fabrication and Characterization of PLA/Nanocrystalline Cellulose Nanocomposite Filaments for 3D Printing Application

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Abstract. 3D process is an additive manufacturing process widely used due to its low cost, high production rates, and ease process. One of the thermoplastic materials commonly used is polylactic acid (PLA). However, PLA has some weakness including low strength and thermal stability. To improve these properties, the addition of the reinforcement materials into the pure PLA must be done and nanocrystalline cellulose (NCC) is one of the potential reinforcement materials. The influence of NCC addition on the tensile and thermal properties of PLA/NCC nanocomposite filament was investigated. NCC was isolated from the ramie fibers using sulphuric acid hydrolysis. Dried NCC powder and PLA pellets were hand-mixed with different NCC concentrations of 0, 1, 3, and 5 wt%. The filament was prepared using a single-screw extruder machine at 185°C under the constant speed. It was found that the diameter of the filament was lower than that of the nozzle of the extrusion machine. The addition of 1 wt% of NCC into the pure PLA increased the tensile strength by 19.04% (from 48.41 to 57.63 MPa) and elastic modulus by 13.47% (from 1791.62 to 2033.07 MPa). The addition of NCC more than 1 wt% decreased the tensile strength and elastic modulus. The optimum NCC loading was achieved at 1 wt%. The presence of NCC had no a significant effect on the thermal stability of the pure PLA.

1. Introduction
Additive manufacturing (AM) technologies, also called as three-dimensional (3D) printing, have been attracting great interest in both industrial and academic fields. This is ascribed from several superior including rapid prototyping, a wide choice of materials, and can produce complex shapes without special tools or moulds [1]. Three-dimensional objects in a layer-by-layer manner can be produced by 3D printing. A lot of devices or systems including robots, prosthetics, orthotics, and skeletal systems can be produced by 3D printing mainly using thermoplastic materials. There are several 3D printing methods such as fused deposition modelling (FDM) or fused filament fabrication (FFF), stereo lithography apparatus (SLA), and electron beam melting (EBM), laminated object manufacturing (LOM), selective laser sintering (SLS), and digital light projection (DLP) [2]. Because of its reliability, simplicity, affordability, minimal wastage, and material availability, FDM is the most widely used 3D printing method [2]. In the FDM process, thermoplastic filament, a conventionally used printable material, is fed to the liquefier head with the pressure generated from a drive gear and a grooved bearing [3,4].
Usually, the most commonly used filament materials are made of pure thermoplastics such as polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), polycarbonate (PC), and polyamide (PA) [5]. However, the final products produced by using these materials have several weaknesses including high cost, low strength, and easy distortion, leading to the limited application of FDM in cost-effective, functional, load-bearing applications as well as in large-scale production [3]. This is attributed to shrinkage during the cooling process, resulting in the warp of the printed products. Moreover, products manufactured by FDM have significantly lower strength than injection moulding due to the formation of voids and poor adhesion between successive layers and adjacent filaments [6]. The addition of reinforcement materials into the pure thermoplastic materials has been well documented to reduce the shrinkage. Accordingly, the development of new composite filaments for FDM is an interesting topic to be developed in the 3D printing industry.

Recently, a lot of composite filaments for FDM has been developed by previous researchers such as ABS/glass fibers, ABS/carbon fibers, ABS/graphene, ABS/nano-clay, ABS/carbon nanotubes, PLA/wood flour, PLA/nano-clay, PLA/carbon nanotubes, PLA/carbon nanoparticles, and polyamide 6/cellulose nanofibrils [2,7,8,9,10,11]. It has been reported that the addition of reinforcement materials into the pure thermoplastic materials increased the mechanical properties. Currently, the use of nanocrystalline cellulose (NCC) as reinforcements in polymers has drawn growing research attention due to its high strength and stiffness, high surface area, low thermal coefficient, distinct rheology, unique optical properties, biodegradable and good biocompatibility [12]. NCC is a nano-sized cellulosic material with the structure of rigid rod-like shaped whiskers with a diameter in the range of 1-100 nm and a length in the range of 10-100 nm [13]. NCC is extracted from native cellulose that can be found from plants (wood and non-wood), marine animals (tunicate), algae, and bacteria [12]. To the best of our knowledge, the filament material based NCC-reinforced PLA has been not yet developed and reported. It is interesting to fabricate the NCC-reinforced PLA filament as an alternative filament for 3D printing application.

In the present study, the NCC-reinforced PLA nanocomposite filaments were prepared by melt-compounding using a single-screw extruder. The effect of NCC addition into the pure PLA on the characteristics and the tensile properties was investigated in this work. The characteristics of the filaments were determined by measuring diameter and Fourier Transform-Infrared spectroscopy. The tensile properties were studied through the tensile test whereas the thermal stability of the filament was characterized by using thermogravimetric analysis (TGA).

2. Materials and Methods

2.1. Materials
Commercial Polylactic acid (PLA) filament used in this study was purchased from Rajawali3D. This filament has 1.75 mm in diameter. Nanocrystalline cellulose (NCC) powder was isolated from the ramie fibers via sulphuric acid hydrolysis as reported by our previously reported [14].

2.2. Methods
First, the PLA filament was cut into about 1-2 mm in length to produce the PLA pellets. The pellets were then dried in the oven at 60°C for 6 h to remove the absorbed moisture within the pellets. Prior to mixing with the PLA pellets, NCC powder was dried using an oven at 60°C for 1 h. Neat PLA and PLA/NCC nanocomposite filaments with different NCC contents (0, 1, 3, 5 wt%) were produced by a single screw extruder (Wellzoom Type B) at a constant screw speed, operating at the temperature of 185°C and the nozzle diameter of 1.75 mm. Filaments were collected using air cooling to obtain a filament diameter of approximately 1.75 mm. The PLA/NCC nanocomposite filaments were characterized using Fourier Transform-Infrared Ray (FT-IR) (IRPrestige21 machine). The diameter of the filaments was measured. The tensile properties of the filaments were determined through the tensile test to obtain the tensile strength, elastic modulus, and elongation at break. The thermal stability of the
filament was investigated using thermogravimetric analyzer (TGA)/differential thermal analysis (DTA). For comparison, the properties of commercial PLA filament was also studied.

3. Results and Discussion

Figure 1 represents the FT-IR spectra of the filaments of pure PLA PLA-0, PLA/NCC with 1 (PLA-1), and 5 wt% (PLA-5) NCC contents. It can be seen that five main peaks could be observed for all samples, namely peaks at 3448, 1751, 1653, 1188, and 1087 cm\(^{-1}\). It is interesting to note that the new peak appeared at 1365 cm\(^{-1}\) for the filament of PLA/NCC nanocomposite containing 5 wt%. The peak at 1365 cm\(^{-1}\) was the characteristic of the sulfonate group. This peak was not found in the PLA-1 sample due to the very low NCC content of 1 wt%. The peak at 3448 cm\(^{-1}\) corresponded to the presence of the hydroxyl (-OH) group which was the identity of cellulose, hemicellulose, lignin, and PLA. The peak at 1751 cm\(^{-1}\) indicates the presence of a carboxylic group C = O which is the identity of hemicellulose, pectin, and PLA. The peak at 1653 cm\(^{-1}\) indicated the presence of the C = C alkane group which is the identity of lignin. The peaks at 1188 and 1087 cm\(^{-1}\) shown the presence of C-O groups from lignin. The intensity of the peak of 1751 cm\(^{-1}\) in PLA-1 was very low due to the very small content of NCC. Meanwhile, in the PLA-5 sample, an increase in peak intensity of 3448 and 1751 cm\(^{-1}\) was caused by an increase in NCC content in the filament.

![Figure 1. FT-IR spectra of the filaments of: (a). pure PLA, (b). PLA-1, (c). PLA-5](image-url)

Figure 2 shows the diameter of the filaments of both commercial PLA and PLA/NCC nanocomposites. It can be seen that the diameter of the commercial PLA filament was 1.75 mm with a very low standard deviation. On the other hand, the filaments of PLA/NCC nanocomposite exhibited a lower diameter with a high standard deviation compared to the commercial PLA one. The diameter of all PLA/NCC filaments was lower than 1.75 mm. The reduction in diameter and heterogenic diameter obtained in all PLA/NCC nanocomposite filaments might be attributed to the shrinkage phenomena during the cooling process from the melting of pellets. Moreover, the unsuitable screw speed in the extrusion process was probably believed to be responsible for the lower diameter of the filaments. In addition, owing to degradation during re-melting might cause a decreased diameter of the filaments.
Figure 2. Diameter of filaments of commercial PLA and its nanocomposites

Figure 3 displays the tensile strength of commercial PLA and its nanocomposite filaments. The tensile strength of the commercial PLA filament is 54.23 MPa while the PLA-0 filament (PLA without NCC) is 48.41 MPa. This indicated that there was a decrease in the tensile strength of pure PLA filament. This was probably associated with the re-melting of commercial PLA indicating the properties degradation of commercial PLA filament. Figure 3 also shows the influence of NCC addition on the tensile strength of PLA/NCC nanocomposite filaments. It can be observed that the tensile strength increased by 19% with 1 wt% NCC addition, but decreased with a further increase of NCC content. The optimum NCC loading was achieved at 1 wt% of NCC resulting in the highest tensile strength. The highest strength obtained at 1 wt% NCC content was probably attributed to the homogeneous dispersion and stronger interaction between the NCC particles and the PLA matrix. The stronger interaction allowed for a better transfer of the applied stress between NCC particles and the PLA matrix leading to the increased tensile strength at 1 wt% NCC content [15]. Furthermore, the reduction in tensile strength in the NCC content more than 1 wt% might be ascribed from the strong tendency of agglomeration of the NCC due to the considerable increase in the inter-particle interaction in the PLA matrix. The agglomerated structures of NCC could be caused by an increase in the number of NCC content resulting in the presence of micro-voids and finally decreasing the tensile strength [15]. Similar findings were also reported by Kariz et al. [7] for wood particle-reinforced PLA filaments and by Papon and Haque [10] for carbon nanofiber-reinforced PLA filaments.

Figure 3. Tensile strength of filaments of commercial PLA and its nanocomposites
Figure 4 presents the elastic modulus of commercial PLA, pure PLA, and its nanocomposite filaments. It can be seen that the elastic modulus of pure PLA filament was higher than that of commercial PLA filament. From Figure 4, it can be also observed that the elastic modulus of the filament increased by 14% from 1792 to 2033 MPa with the presence of 1 wt% NCC, but then decreased with higher levels of NCC content to 1541 MPa for the filament with the 5 wt% NCC content. This trend resembled that of tensile strength. The maximum value of elastic modulus was found at the 1 wt% NCC content. The highest elastic modulus at 1 wt% NCC might be also associated with the homogeneous dispersion and better interfacial interaction between NCC and the PLA matrix. The addition of NCC more than 1 wt% decreased drastically the elastic modulus of the filaments. This reduction was again probably ascribed from the presence of agglomeration of NCC at a higher level of NCC content that acted as the preferential sites for the crack initiation and failure led to the reduced elastic modulus [15].

Figure 4. Elastic modulus of filaments of commercial PLA and its nanocomposites

Figure 5 illustrates the influence of NCC addition on the elongation at break of the PLA/NCC filaments. The elongation at break for commercial PLA is also demonstrated for comparison. From Figure 5, it can be seen that the filament of commercial PLA exhibited a higher elongation at break than that of PLA/NCC nanocomposite filaments. In the other words, the ductility of commercial PLA filament was higher compared to that of PLA/NCC nanocomposite filaments. This was attributed to the presence of NCC stiff particles limited to the PLA matrix deformation and then resulted in the reduced ductility. As shown in Figure 5, the elongation at break of the filaments increased with increasing NCC content up to 3 wt% and then decreased for a future increase of NCC loading.

Figure 5. Elongation at break of filaments of commercial PLA and its nanocomposites
The thermal stability of the filaments of pure PLA and its nanocomposites containing 1 and 5 wt% of NCC is characterized using the thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) with the results presented in Figures 6 and 7, respectively. The analysis of the results of TGA and DTG curves are summarized in Table 1. It can be seen from Figure 6 that the only main stage of weight loss is observed in the range temperature of 290-370°C, corresponding to the structural decomposition of the PLA chains. The thermal stability can be determined from the onset temperature of major decomposition (T₀) and its values as summarized in Table 1. From Table 1, it can be found that the T₀ values of the filaments of pure PLA and its nanocomposites with 1 and 5 wt% are 300, 298, and 290°C, respectively. This indicated that the addition of NCC decreased slightly the thermal stability. The reduction was probably attributed to the presence of sulphate groups on the NCCs surface during sulphate acid hydrolysis that accelerated the degradation [16]. Moreover, the small NCC loading into the pure PLA might be believed to be responsible for the decreased thermal stability. A similar observation was also reported by Tao et al. [2] where it was found that the addition of wood flour had little effect on the thermal stability of the filament of PLA/wood flour composites. This was due to the lower thermal decomposition temperature of wood flour and the thermal decomposition residual ratio was higher than that of PLA. From Table 1, it can also be seen that the residual weight of the filaments of PLA/NCC nanocomposites at 600°C is higher than that of pure PLA. This was probably associated with the presence of volatiles produced in the PLA/NCC nanocomposites.

Furthermore, Figure 7 displays the DTG curves of the filaments of pure PLA and its nanocomposites. From this figure, the degradation temperature on the maximum weight loss rate (Tₘₐₓ) can be determined and the results as presented in Table 1. The Tₘₐₓ values of the filaments of pure PLA and its nanocomposites containing 1 and 5 wt% are 347, 346, and 350°C. This indicated that there was no different degradation peak temperature in all samples. In other word, the thermal stability of pure PLA was not significantly affected by the presence of NCC. These results were in consistent with the TGA results.

The thermal stability of the filaments was also investigated through differential thermal analysis (DTA) as shown in Figure 8. DTA is one of the characterization methods to measure the thermal properties such as melting, phase transition, sublimation, and decomposition of the material related to the temperature change of the materials. From Figure 8, it can be observed that all samples showed two weak endothermic peaks at around 65 and 166°C and a sharp endothermic peak at around 353°C. The weak endothermic peak at around 65 corresponded to the glass transition temperature while a weak endothermic peak at around 166°C represented the melting point of the pure PLA [17]. The sharp endothermic peak at around 350 represented the decomposition or degradation of pure PLA chains. All samples exhibited a similar endothermic peak indicating no effect on the thermal stability due to the addition of NCC into the pure PLA. This trend is similar to the TGA and DTA results as shown in Figure 6 and 7. It can be concluded that the thermal stability of the pure PLA unchanged with the presence of NCC.
Figure 6. TGA curves of filaments of pure PLA and its nanocomposites with 1 and 5 wt% of NCC

Table 1. Onset temperature ($T_o$), degradation temperature on the maximum weight loss rate ($T_{max}$) and char yield ($W_{residue}$) of pure PLA and its nanocomposite filaments containing 1 and 5 wt% of NCC obtained from the TGA and DTG curves

| Sample | TGA | DTG |
|--------|-----|-----|
|        | $T_o$ (°C) | $W_{residue}$ (%) | $T_{max}$ (°C) |
| PLA-0  | 300  | 1.33 | 347 |
| PLA-1  | 298  | 1.75 | 346 |
| PLA-5  | 290  | 1.76 | 350 |

Figure 7. DTG curves of filaments of pure PLA and its nanocomposites with 1 and 5 wt% of NCC
Figure 8. DTA thermographs of filaments of pure PLA and its nanocomposites with 1 and 5 wt% of NCC

4. Conclusion
The NCC-reinforced PLA nanocomposite filaments with different contents of NCC were successfully produced through melt-compounding using a single screw extruder. The diameter of NCC-reinforced PLA nanocomposite filaments was inhomogeneous and lower than that of commercial PLA filament. The addition of NCC had a significant effect on the tensile properties, while the unremarkable effect on thermal stability. By the addition of 1 wt% NCC content, the tensile strength and elastic modulus increased by 19 and 14%, respectively. However, the tensile strength and elastic modulus decreased for a further increase in NCC content. The thermal stability of the filament of the PLA matrix unchanged by the presence of NCC. The filament of NCC-reinforced PLA has great potential for alternative filament materials for 3D printing application owing to its higher mechanical properties.

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