Fabrication of Thermoplastic Nanocellulose Composite Material

D. -Y. Lim*, J. -A. Lee and K.-Y. Kim

Korea Institute of Industrial Technology, Ansan-si, Gyeonggi-do, Korea
*zoro1967@kitech.re.kr

ABSTRACT

Nanocellulose fibers with the average diameter below 100 nm were successfully obtained by a high pressure homogenizer. The large surface areas and nano-scale dimensions of the nanocelluloses can lead to the emerging materials for reinforcements in the polymer composites. The nanocellulose was differentiating from common polymer composites and providing the opportunity for nano-engineered materials that could have not achieved from conventional materials. In our previous work, the wet-laid process was found a good method to make nano-cellulose/polyamide 6 nanocomposites. We investigated the fabrication of composite material. Also, we compared the effects of the shape of materials. The low-viscosity poly-amide 6 meltblown nonwoven showed the suitable perfor-mance as a matrix material.

Keywords: nanocellulose, thermoplastic composites, melt-blown nonwoven, wet-laid process, homogenizer

1 INTRODUCTION

Recently, the use of cellulose fibers as the reinforcing materials in the polymeric matrices has gained a great attention in engineering applications due to their low density, low cost, renewability and recycleability as well as excellent mechanical properties such as high flexibility, sepcific tensile strength and modulus [1]. In the polymer composites manufacturing industries, the cellulose rein-forced composites are considered as the environmental friendly materials for substitution of the conventional and non-renewable reinforcing materials, such as carbon, glass or aramid fibers used for the packaging, construction and automotive industrial fields [2]. Nowadays about 50% of internal parts of vehicle are made of polymeric composites [3]. According to the estimation of the Corporate Average Fuel Economy, a 10% reduction in weight of a car can decrease fuel usage by 6~8%. The higher volue fraction of lower density natural fibers in the plastic composites can significantly reduce the weight of the final product. Especially, the reinforcement by cellulose nanofibers (CNFs) instead of micro-sized fibers is recognized as being more effective due to interactions between the nano-sized elements that make up a percolated network connected by hydrogen bonds or entanglements, once a good dispersion in the matrix is achieved [4].

The CNF is a form of expanded high-volume cellulose, moderately degraded and greatly expanded in surface area, obtained through a high pressure homogenization process. Passing the cellulose suspension through the homogenizer for several times, the cellulose fibers are splitted to nanosized fibrils and the final CNF diameters are ranges from 10 to 100 nm. The large surface area, thermal and dimensional stability of CNFs are useful for improvement of mechanical property of CNF reinforced composites. However, the CNFs still have low compatibility with polymeric matrices and it can be affect on degrading of the mechanical properties [5]. There are some literatures about the new production method of the composites which are composed with hydrophilic cellulose and hydrophobic polymer. In the previous study [4], a new fabrication system similar to papermaking, which enables the production of thin sheets made of uniformly dispersed CNF with polylactic acid (PLA) fibers is developed. This process is suitable for application at an industrial field due to the high production yields and fast dewatering times.

In the composites of CNFs and polymeric matrices, the effects of the chemical treatment (silane coupling agent, retention aid and chemical modification) [6], additives (compatibilizer, nanoparticle and binder) [1,7] and physical treatment (entanglement) [7] on the thermal, structural and mechanical properties have been widely studied. However, there is little research on the effect of the geometrical structures of matrices materials on the microstructures and mechanical properties of the composites. There is also a few researches about the manufacturing method of CNF reinforced polyamide (PA6) multi-layered composites.

In this study, the CNFs are manufactured uniformly by the wood pulp and homogenizer and the CNF/PA6 sheets are manufactured by our wet-laid sheet forming process. For investigation of gyometrical structural effects of the matrices and CNF contents to the morphological and mechanical properties (tensile, flexural and fatigue properties) of the composites, the multi-layered CNF/PA6 composites are fabricated from the various shapes of matrices (low melting meltblown nonwoven, PA6 film and low viscosity PA6 meltblown nonwoven) and CNF contents.

2 EXPERIMENTAL

2.1 Materials

The hardwood pulps (fiber length: 1.0 mm) are used to prepare the CNFs by homogenization process. The PA6 fibers (fiber length: 1.0 mm, fineness: 1.5 denier) are used for manufacture the CNF/PA6 sheets. Three kinds of matrices are applied for this study as following: (1) low melting meltblown nonwoven (17 g/ m^2), (2) PA6 film (17 g/ m^2, 15 μm), (3) low viscosity PA6 meltblown nonwoven (100 g/ m^2).

2.2 Preparation of CNFs

The mechanical pretreatment of woodpulps by pulper is performed at the immersing condition and mixing in tap water for 30 minutes (woodpulp 2 g in water 1 L). The resulting slurry is subject to the high pressure homogenizer (Mini deBee, Bee International, USA) for fibrillation of the cellulose fibers at the reverse nozzle setup. The CNF slurry is totally fifteen times through the homogenizer with three kind of nozzle sizes at different operating pressures. The first five passes are carried out an operation pressure of 70 MPa with a nozzle of 250 μm diameter, and then the second five passes at an operation pressure of 240 MPa with a nozzle of 200 μm diameter and the last five passes at an operation pressure of 310 MPa with a nozzle of 150 μm diameter.

2.3 Preparation of CNF/PA6 sheets

After homogenization process, the CNF/PA6 sheets are prepared by wet-laid hand sheet former from the CNFs slurry and PA6 fibers using a 1,000 grade stainless steel mesh. For fabrication of the CNF/PA6 sheets containing the 40 wt.% CNF, the PA6 fibers (1.8g) adds into the CNF slurry (240 g). The collected CNF/PA6 sheets are pressed for dewatering at 80℃ and 3.4 MPa for 2 hrs. and then dried at 80℃ for 12 hrs. in a convection oven under the ambient pressure. The final CNF/PA6 sheets are calendered under the pressure of 4.8 MPa at 210℃ and a feeding speed of 0.5 m/min.

2.4 Preparation of multi-layered CNF/PA6 composites

The CNF/PA6 sheets are used for manufacture of the multi-layered CNF/PA6 composites. For investigation of the effect of matrices shapes on the mechanical properties of CNF/PA6 composites, the low melting meltblown nonwoven, PA6 film and low viscosity PA6 meltblown nonwoven are used as the matrices from 2 to 5 layering structures. Figure 1 shows the preparation process of the multi-layered CNF/PA6 composites. The matrices materials are located between the each layers.

Table 1 shows the pressing and melting conditions for adhesion of the each layers, number of layers, CNF contents, total thickness and sample codes of the multi-layered CNF/PA6 composites used in this study. The hot press is used for adhesion of each layers by pressing (30 MPa) at the each heating temperature and treatment time.

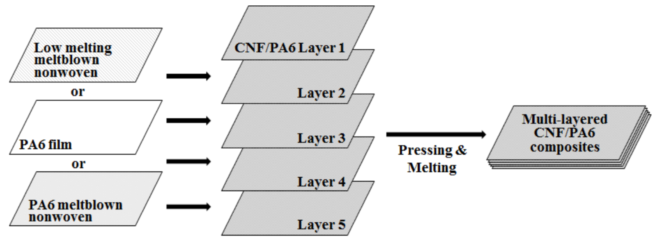


Figure 1: Preparation process of the multi-layered CNF/ PA6 composites with various matrices.

Table 1: Manufacturing conditions, number of layers, CNF contents and total thickness and sample codes of the multi-layered CNF/PA6 composites.

Matrix	Manufac-turing condition	Number of layers	CNF content (wt.%)	Total thickness (mm)	Sample codes
PA6	-	1	0	0.20	P1
CNF/PA6 sheet	-	1	40.0	0.04	N1
Low melting meltblown nonwoven	230℃/ 60sec.	2	37.5	0.16	L2
		3	36.7	0.28	L3
		4	36.3	0.40	L4
		5	36.1	0.49	L5
PA6 film	150℃/ 120sec.	2	37.5	0.17	F2
		3	36.7	0.29	F3
		4	36.3	0.40	F4
		5	36.1	0.54	F5
PA6 meltblown nonwoven	230℃/ 60sec.	2	37.5	0.26	M2
		3	36.7	0.42	M3
		4	36.3	0.62	M4
		5	36.1	0.83	M5

2.5 Mechanical Testing

The tensile tests are conducted according to the ASTM D 638-03. The tensile behavior of the CNF/PA6 composites is measured using an universal testing machine (H100KS, Tinius Olsen, UK) with a 2.5 kN load cell and the test speed is 1.0 mm/min.

The flexure tests are conducted according to ASTM D 790-03, that is, three-point loading system using center point loading by universal testing machine with 2.5 kN load cell and the displacement rate is 1.0 mm/min.

The axial loading tension fatigue tests are carried out according to ASTM D 671-71 using the electrodynamic test system (MTS Acumen 1, MTS system Corp. USA) with 3.0 kN load cell. The maximum cyclic stress in the outer fiber is calculated by the maximum load values of tensile test results. From the 80% to 30% of the maximum load values are applied to measure the number of cycles for fatigue failure under the given cyclic loadings of the CNF/PA6 composites.

2.6 Morphology

A field emission scanning electron microscopy (FE-SEM, SU8010, Hitachi, Japan) is used to investigate the microstructures of the multi-layered CNF/PA6 composites. The fracture surfaces of CNF/PA6 composites are analysed after tensile test. The samples are coated with osmium before imaging using an auto fine coater.

3 RESULTS AND DISCUSSIONS

3.1 Tensile properties

Figure 2 shows the tensile strength of the neat PA6 and CNF/PA6 composites with layers and matrices. The composites reinforced with CNFs displays enhanced tensile properties in comparison with the neat PA6 sheet. Because of better stress transfer properties of CNF/PA6 composites, the tensile strength is increased (reaching a value 46.9 MPa with the 36.3 wt.% CNF content). In the case of sample (L) and (f), the tensile strength is increased as the CNF content increasing. However, the tensile strength of sample (M) is increased with decreasing of the CNF content. It seems that the structural property of matrix of PA6 meltblown nonwoven affect the tensile strength of multi-layered CNF/PA6 composites.

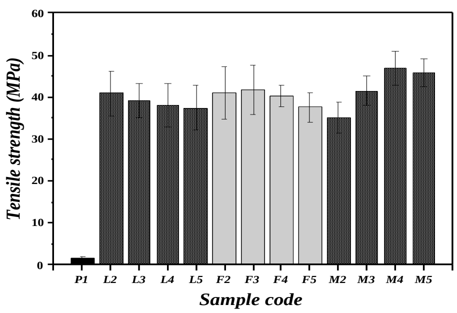


Figure 2: Tensile strength of multi-layered CNF/PA6 composites with shape of matrix.

The effect of CNFs on the elongation at break of PA6 is shown in Table 2. As shown in Table 2, the elongation at the break for the composites increased with increasing CNF content. It means that the CNFs are uniformly dispersed in the PA6 matrix. Increase of the elongation break indicates the capability of the CNF to support the stress transfer from CNF to matrix [3].

Table 2: Summary of mechanical properties of multi-layered CNF/PA6 composites with CNF content.

Sample codes	CNF content (wt.%)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (GPa)
P1	0	1.6	0.8	0.8	-	-
N1	40.0	64.9	5.0	5.14	-	-
L2	37.5	40.8	2.9	5.0	47.6	0.9
F2		41.0	2.6	5.4	36.8	1.1
M2		35.2	2.4	5.6	27.7	1.3
L3	36.7	39.1	3.0	4.6	44.2	1.1
F3		41.8	2.6	4.6	42.2	1.5
M3		41.5	2.6	5.1	38.8	1.6
L4	36.3	38.1	2.8	4.7	39.3	1.2
F4		40.3	3.1	4.6	42.8	1.9
M4		46.9	2.7	4.8	62.2	2.0
L5	36.1	37.5	2.9	4.6	33.9	1.3
F5		37.6	3.4	3.9	42.8	2.5
M5		45.7	3.0	4.1	79.9	2.7

Figure 3 shows the tensile modulus of neat PA6 sheet and CNF/PA6 composites with layers and matrices. The tensile modulus of CNF/PA6 composites systemically increased with increasing CNF content. As the CNF content decreased, the tensile modulus of CNF/PA6 composites increased due to increase of stiffness.

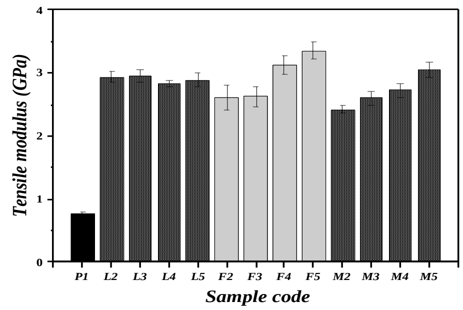


Figure 3: Tensile modulus of multi-layered CNF/PA6 composites with shape of matrix.

3.2 Flexural properties

The effect of different amount of CNF content and matrix shape on the flexural strength is shown in Figure 4. The neat PA6 and CNF/PA6 sheet can not measured the flexural strength. As the CNF content increased, the flexural strength is also increased in the sample (L) and (F). Similar to tensile strength result, the flexural strength of sample (M) is increased with decreasing of CNF content and increasing of layers. This phenomenon is caused by structural characteristic of PA6 meltblown nonwoven. The increase in flexural strength of multi-layered CNF/PA6 composites can be attributed to a well-formed interface that allows better stress transfer from matrix to the CNF.

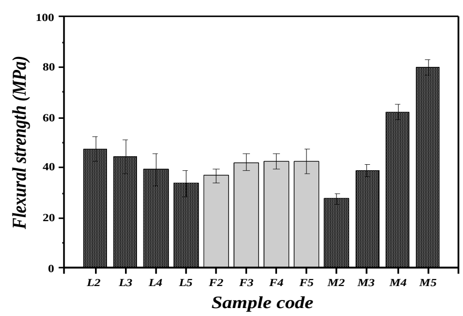


Figure 4: Flexural strength of multi-layered CNF/PA6 composites with shape of matrix.

Figure 5 shows the flexural modulus of multi-layered CNF/PA6 composites with shape of matrix and the number of layers. The flexural modulus is decreased with CNF content increasing. When the PA6 film and meltblown nonwoven are used as the matrices of CNF/PA6 composites, the flexural modulus is largely increased with stiffness increasing. The composite stiffness increasing is depends on the CNF content and uniformity of CNF dispersion [3].

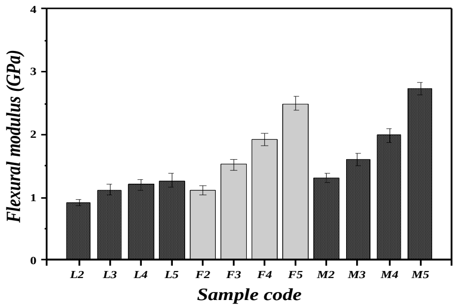


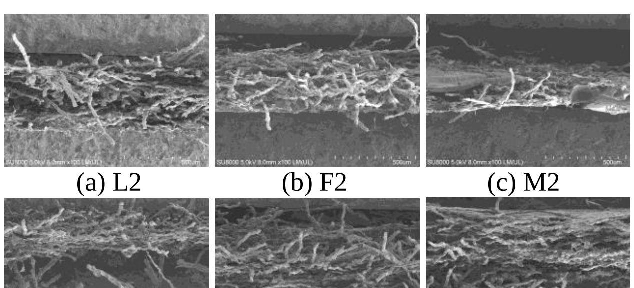
Figure 5: Flexural modulus of multi-layered CNF/PA6 composites with shape of matrix.

3.3 Fatigue properties

The fatigue tests usually involve the determination of the number of cycles for fatigue failure at different flexural or tensional forces. Fatigue failure is occurred when (a) the sample breaks in two pieces; (b) for some fiber filled composites, by formation of a single crack or generla cracking; (c) by decay of the modulus of elasticity to 70% of the original odulus (ASTM D 671-71 test method); (d) the specimen residual strength is reduced to the value of maximum cyclic stress [8]. In this study, there is no fatigue failure of the types mentioned but only fatigue damage. According to the stresses to the sample, the cracks are occurred with surface orginating type, interior orginating type and fish eye type.

3.4 Morphology

Figure 6 shows the fracture structures of 2 and 5-layered CNF/PA6 composites with different matrices shapes. In the 2-layered CNF/PA6 composites, the interfaces between the layers are not distinguished. However, the interfaces among the inner layers of 5-layered CNF/PA6 composites are clearly differentiated, especially in the center parts. The pressure and the temperature applied from the outermost layers are not reach into the innermost part.


(a) L2 (b) F2 (c) M2

(d) L5 (e) F5 (f) M5

Figure 6: Fracture structure of 2 and 5-layered CNF/PA6 composites with shape of matrix.

Therefore, the matrices existed in the inner part of multi-layered CNF/PA6 composites are not fully melted and it brought about the poor interfacial adhesion among the inner fibers and matrices. In the 2 and 3-layered CNF/PA6 composites, the interfacial delamination is not observed. When the PA6 film used as the matrix, the separating effect between the layers of the CNF/PA6 composites is appeared specifically.

Figure 7 shows the surfaces of the inner fibers of multi-layered CNF/PA6 composites with different matrices shapes. In Figure 7(a), the CNFs are adhered to the surface of PA6 fibers in the CNF/PA6 sheet. The low melting meltblown nonwoven is permeated into the voids of among the fibers effectively, as shown in Figure 7(b). The PA6 film in Figure 7(c) is fully melted and it clung to the surface of fibers and the pores in the CNF/PA6 composites are still existed. The PA6 meltblown nonwoven is melted in the multi-layered CNF/PA6 composites and it filled up the inner pores and connected inner fibers each other, as shown in Figure 7(d). From the morphological analysis, the meltblown shape matrices are suitable for the multi-layered CNF/PA6 composites.

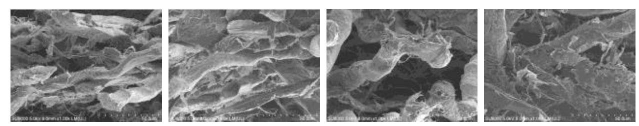

(a) N (b) L (c) F (d) M

Figure 7: Fiber surface in the multi-layered CNF/PA6 composites with shape of matrix.

4 CONCLUSIONS

The multi-layered CNF/PA6 composites are sucessfully manuractured with various matrices shapes and CNF contents. The composites reinforced with CNF displays enhanced tensile, flexural and fatigue properties in comparison with the neat PA6 sheet. The matrix shape is affect the mechanical properties of CNF/PA6 composites due to its structural characteristic. In this study, the PA6 meltblown nonwoven is the most suitable matrix for multi-layered CNF/PA6 composites among the using matrices. Development of multi layering technology for CNF reinforced composites will extend the application in the automotive and other applications for replacing of glass fiber because of both environmental and economical benefits.

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