PCL/PEO Composite Nanofiber Manufacturing Technology Using Air Jet Spinning Method

Eun Ji Kuk, Myung Goo Hwang, Myung Geun Kim, Sang Bum Kim,
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***Abstract*—**This study woven PCL by different concentrations using Air Jet Spinning Method(AJS), observed the surface and manufactured nano-fiber under the optimal condition.

PCL is cheap with superior processability and lots of studies on it have been conducted as a biodegradable material without any toxicity. In comparison with other biodegradable high molecule, the speed of degradation is slow. So, there are weaknesses that it's mainly used for the system of organ drug transfer or has low mechanical characteristics.

To improve mechanical characteristics of PCL nano-fiber manufactured by Air Jet Spinning method, nano-fiber was manufactured by blending PEO. PCL/PEO blending nano-fiber showed increased tensile strength and hydrophilicity respectively.

***Keywords*—** Nanofiber, Polymer, Air jet spinning, PCL, PEO

I. INTRODUCTION

BIODEGRADABLE polymers are chemically degradable by the microbiological activities existing in the nature, so biodegradable polymers are eco-friendly and unharmful to your body. Therefore, studies about biodegradable polymers are actively being researched, now.[1] PLA(polylactic acid) is one of the biodegradable polymers widely used, but they are not suitable as a material requires flexibility because they are expensive and crystallization temperature is high.[2] PCL(polycaprolactone), as one of the aliphatic polyester derivatives that are similar to PLA in structure, is chemical free and nontoxic with relatively low in price. Also, PCL is a hydrophobic biodegradable polymer which is more flexible than PLA. The melting point of PCL is as low as 60℃, which makes it easy to fuse with other polymers and excellent to manufacture with slow speed of dissolution. Thus, PCL has been used in surgical staplers and studies such organ chemical transportation system. However, mechanical property of PCL is poor.[3] To improve the weakness of PCL, manufactured fibers with air Jet Spinning by blending with hydrophilic polymer, PEO(Polyethylene oxide), to confirm the changes in mechanical property. The diagram of Air Jet Spinning(AJS) technique and AJS devices are shown in Fig. 1.[4,5]

AJS technique, a fiber spinning method, spins the solution only with air pressure, so the solvent gets evaporated before the solution reaches the basic materials and only the material expected to be spined is left and produce a sheet. Compare to electricity spinning, since it does not need conductivity required by the basic materials, wide coating on various basic materials is possible, manufacturing speed of fibers is fast and simple at low cost.(6)

In this study, we are to find optimal condition of concentration by spraying nano fiber of PCL with AJS technique, and manufacture PCL/PEO sheet with increased mechanical features by comparing to nano fibers sprayed by blending PEO.

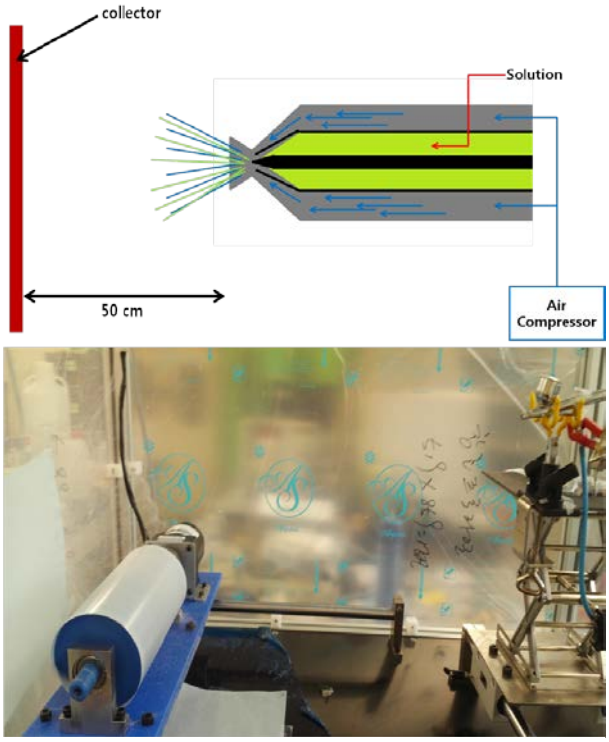

Fig. 1 Schematic diagram of Air jet spinning method and the device

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II. Experimental

A. Manufacturing solution

The polymers used in AJS are PCL with 80,000 MW and PEO with 100,000 MW purchased from Sigma-Aldrich, commonly used dichloromethane (DCM, Sk chemical, Japan) as a solvent of polymers. PCL solutions were manufactured in 5, 7, 10 wt%, and PEOs were 5, 7, 9 wt% to make each fiber. We manufactured the solution by blending PCL 7 wt% and PEO 9wt% with the ratio of 75/25.

B. Manufacturing fiber

We did spinning fiber method by using AJS technique, and the conditions for AJS are 450 kPa, 50cm of distance to the basic material with temperature and humidity of 25(±2) ℃, 30(±3)%, relatively. Solution was kept in the vacuum oven at 40 ℃ for 24 hours to remove residual solvent after spinning the fiber at the spinning speed of 10ml/h.

C. Analysis of properties

C.1 surface analysis

To observe surfaces of PCL and PEO, the nano fibers, we selected the optimal concentration of the fiber and the type of PCL and PEO nano fibers by using FE-SEM(SU-10, HITACHI, JAPAN).

C.2 Analysis of crystallization· atomic combination

To estimate phase change and the degree of crystallization of manufactured PCL, PEO, PEL/PEO polymer nano fiber used XRD(MAX-2500, Rigaku, Japan), set the estimating range of 5°~50° on Cu target. To confirm the molecular composition of the materials, we analyzed unique spectrum of the materials by using FT-IR(Spectrum GX, Perkin Elmer, USA).

C.3 Analysis on mechanical features

We checked if the hydrophilic property of the manufactured fiber from the average value of 5 different attempts by using the contact angle measurement device(GBX, Digidrop, France) is increased or not. And, we measured the tensile strength and elasticity at the speed of 5mm/min with using UTM(Universal Testing Machine, UK).

III. Results and Discussion

A. Surface properties

We observed surfaces of the fiber by using FE-SEM to find out the optimal concentration of PCL and PEO nano fibers manufactured with the AJS technique. In Fig 2 and Fig 3, each shows the picture of the surface of nano sheet manufactured at different concentrations of PCL and PEO. In Fig 2, PCL fiber manufactured at 5 wt% has formed some fibers but the composition is not even and the diameter is not regular. Even if it is a small amount, beads were formed, and the end of the fiber is disconnected. In the meanwhile, PCL fiber manufactured at 7 wt%, average diameter is about 500 nm, which is relatively regular and the arrangement is very even, which leads us to conclude that it is a well made fiber. Although PCL manufactured at 10 wt% is with low ratio, any formats of the fiber was not shown and it was not suitable for manufacturing

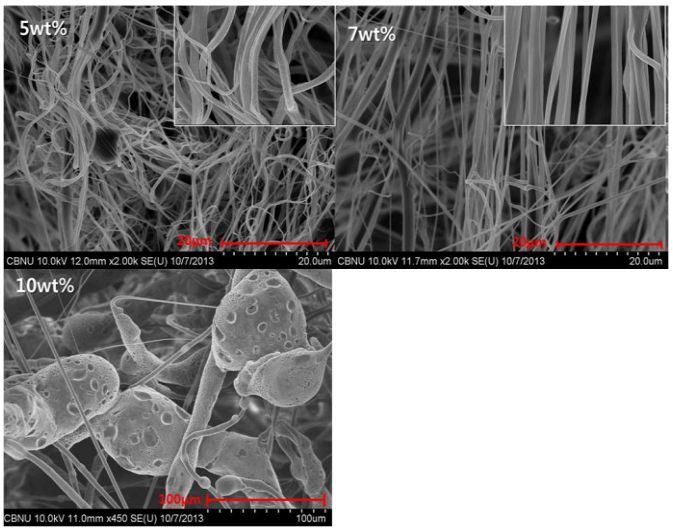

Fig. 2 FE-SEM image of PCL fibers using AJS method. The insets display their high magnification image.

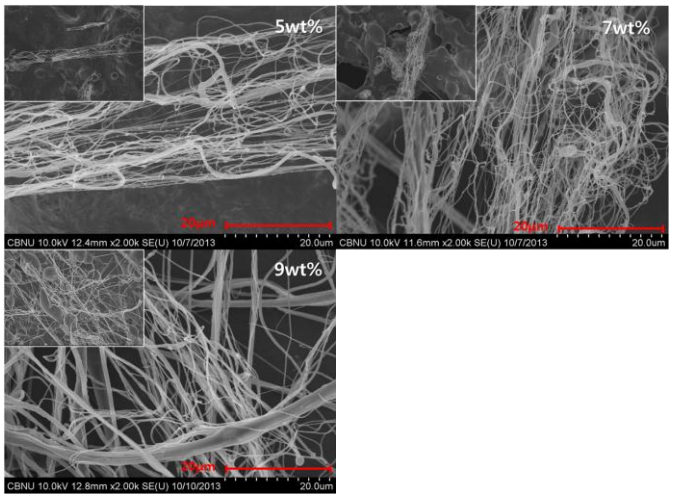

Fig. 3 FE-SEM image of PEO fibers using AJS method. The insets display their low magnification image.

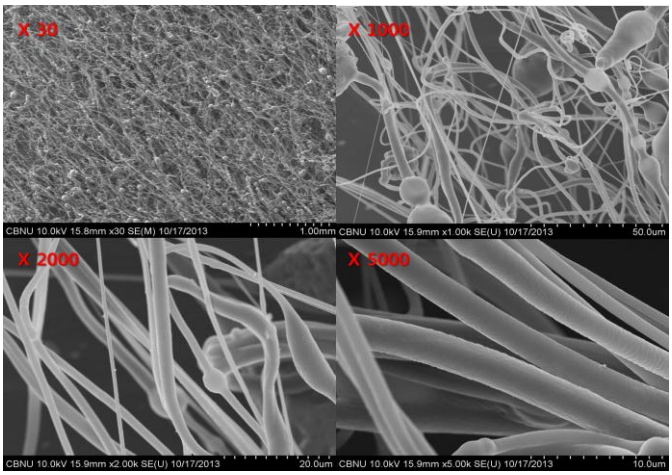

Fig. 4 FE-SEM image of PCL/PEO blending fibers using AJS method.

nano fiber sheets.

Fig 3 is the picture of surface of PEO spined with AJS technique. Overall, PEO could not accomplish the regular fiber

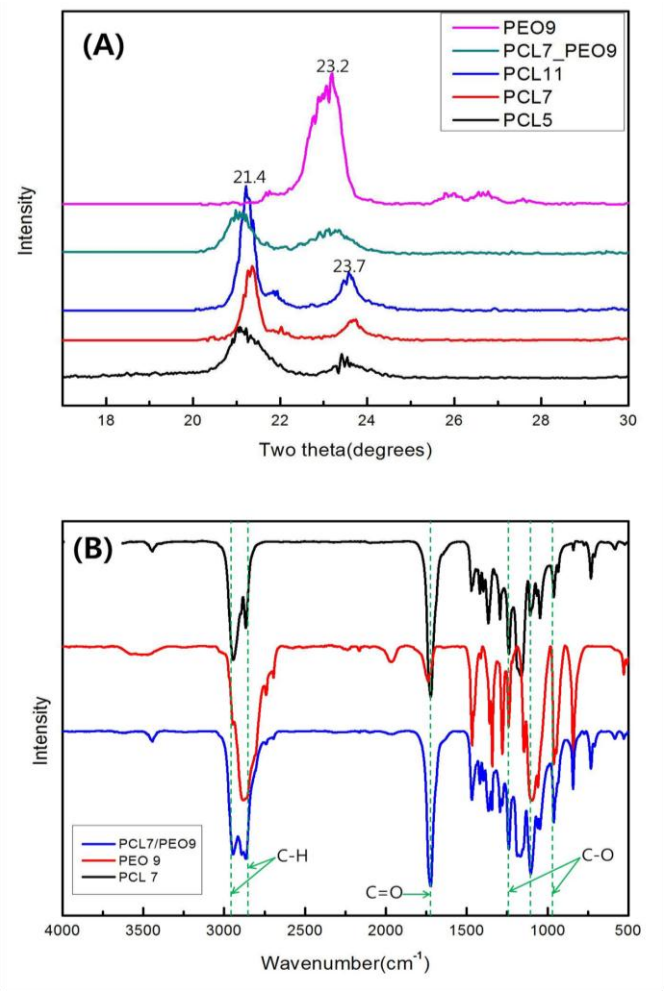

Fig. 5 XRD patterns of (A) PCL, PEO and PCL/PEO fabricated membrane, and (B) IR spectra of PCL, PEO and PCL/PEO membrane samples.

spinning. Once you look at the picture that has overall surface, there is a tendency of forming fiber on top of slight coating of PEO. Formation of the fiber increases as the concentration of the solution increases.

With a ratio of 75/25 of blending PCL 7 wt% and PEO 9 wt%, we manufactured complex nano fiber. Fig 4 shows the fiber spined with PCL/PEO blended solution. The fiber was formed relatively more stable and regular compare to spinning PEO only, but beads are formed a lot compare to PCL fiber, and the diameter of the manufactured fiber was as thick as 2 μm.

B. The degree of crystallization and atomic combination

Fig 5A shows XRD pattern of the manufactured fiber with PCL, PEO, and PCL/PEO and Fig 5B shows the IR spectrum. Based on the analysis shown in Fig 5, PCL solution shows the peak at around 21.4°, 23.7°. As the concentration increases, the width of the peaks gets narrower, and intensity increases. The height of the peaks are proportional to the concentrations of the solutions, and as the narrower width of the peaks means better crystallization. In this graph, as the concentration increases, crystallization gets better. PEO solution shows maximum peak at 23.2°. In the PCL/PEO blending solution, above 3 peaks are all shown, but the degree of crystallization got lowered.

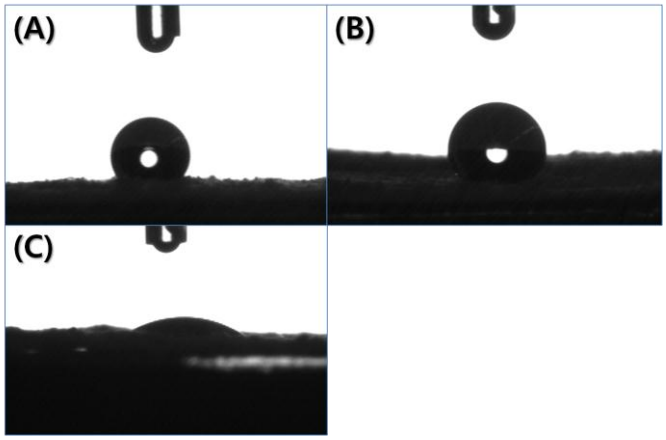

Fig. 6 Images of contact angles of (A) PCL, (B) PCL/PEO and (C) PEO membrane.

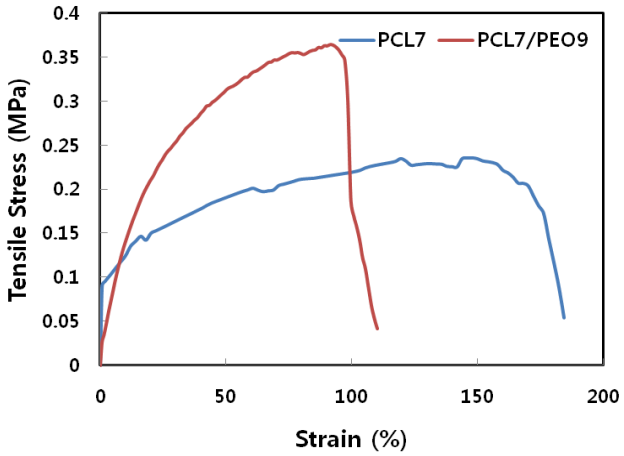

Fig. 7 Stress-strain curves obtained from tensile tests on AJS-fabricated membranes.

However, new crystallization was not formed based on the fact that new locations of the peak were not shown up. IR spectrum in Fig 5B, H-bond between PCL and Aliphatic aldehyde(C-H) of PCL, and these two properties are all shown up as wide absorption band and 2 weak peaks in PCL/PEO blending solution. As PCL and PEO get blended, carbonylic(C=O) peak of PCL/PEO gets stronger, which means that the reactivity gets sufficient. C=O bond is not disconnected but maintained the same as the status before PCL/PEO were blended.

C. Mechanical properties

In Fig 6, it shows contact angulation measured to find the hydrophilic property of the manufactured polymers with AJS technique. Contact angulation with hydrophobic PCL fiber was average 127°, and hydrophilic PEO fiber was average 48°. The contact angulation of PCL/PEO blending fiber was 118°, which mean more hydrophilic property compared to PCL fiber.

Fig 7 is a graph shows the tensile strength of the manufactured fiber. PEO sheet, manufactured with AJS

TABLE I
SUMMARY OF DATA OBTAINED FROM STRESS-STRAIN CURVES.

Sample	Tensile strength (MPa)	Breaking elongation (%)
PCL 7	0.211±0.027	150±12
PCL7/PEO9	0.293±0.072	91±8

Technique, does not have the mechanical strength to measure the tensile strength. We recorded the mechanical strengths of PCL sheet and PCL/PEOL blended sheet measured. Tensile strength of PCL/PEO blended sheet has 72% increased tensile strength compared to PCL solo sheet, and the stretch ratio decreased by 60%.

IV. CONCLUSION

In this study, we manufactured polymers such as PCL, PEO, and PCL/PEO fiber with AJS technique.

(1) When PCL fiber has 7 wt% concentration with AJS technique, even fiber of 500nm was manufactured.

(2) In PEO fiber, when the concentration is at 9 wt%, the fiber is formed, relatively stable. As the concentration increases to a certain level, the number of beads decreases and the diameter increases.

(3) PCL7/PEO9 blending fiber has increased hydrophilic property compared to PCL solo fiber. Tensile strength of PCL7/PEO9 blending fiber was increased, but the stretch ratio was decreased.

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