

미결합 고분자가 없는 poly(L-lactide)-graft-carbon nanotube의 합성

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Synthesis of poly(L-lactide)-graft-carbon nanotube free from unbound polymers

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INTRODUCTION

The preparation of polymer-carbon nanotube composites is one of the most promising alternatives to the conventional filled polymers. The dispersion of the nanometer-sized carbon nanotubes in a polymer matrix leads to markedly improved physical properties of the polymer. Because of the environmental concerns, this approach has also been applied to the biodegradable and biocompatible synthetic aliphatic polyesters such as poly(lactic acid) (PLLA). Indeed, the performance of these polymers can be greatly enhanced, which could make them good competitors for the commodity materials such as engineering plastics, while keeping their complete biodegradability.¹⁻³

In the present study, poly(L-lactide)(PLLA) chains were grafted to multi wall carbon nanotubes(MWNT) by the ring opening polymerization of L-lactide in the presence of MWNT functionalized with hydroxy groups(MWNT-OH).

The amount of the PLLA chains grafted to MWNT-OH could be controlled by adjusting the polymerization conditions.

EXPERIMENTAL

Materials. L-lactide was purchased from PURAC. They were dried under vacuum before use. Triisobutylaluminum(AIBt₃) was purchased from Aldrich. AIBt₃ solutions were stored in a glass ampoules under nitrogen atmosphere. The multiwalled carbon nanotube (MWNT) was obtained from Iljin Nanotech (Korea). Hydroxy groups were introduced to MWNT in our group as follows:

Acid Treatment of the MWNT. A 500mL flask charged with 2.5g of crude MWNT and 200mL of 60% HNO₃ aqueous solution was sonicated in a bath (28 kHz) for 30 min. The mixture was then stirred for 12h under reflux. After cooling to room temperature, it was diluted with 400mL of deionized water and then vacuum-filtered through a 0.22 μ m polycarbonate membrane. The solid was washed with deionized water until the pH of the filtrate reached about 7. The solid was then dried

under vacuum for 12h at 60°C to give 1.5g (~60%) of carboxylic acid-functionalized MWNT (MWNT-COOH).

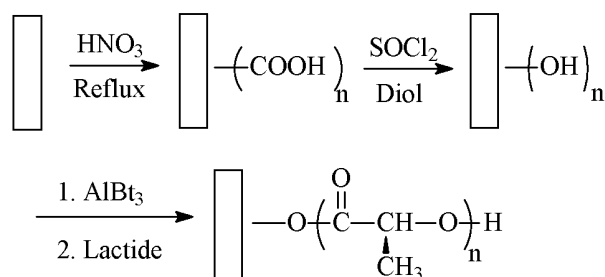


Figure 1. The route for the synthesis of PLA graft MWNTs

Synthesis of MWNT-OH. Dried MWNT-COOH(0.5g) was suspended in 20mL of SOCl_2 and stirred at 65°C for 24h. The solid was then separated by the filtration and the unfiltered residue was washed with anhydrous THF. Subsequently, it was dried under vacuum at room temperature for 2h to give 0.45g of acid chloride functionalized MWNT(MWNT-COCl). The MWNT-COCl was mixed with 20mL of ethylene glycol and stirred at 120°C for 48h. The solid was separated by vacuum filtration using a 0.22 μm polycarbonate membrane as mentioned above and washed with anhydrous THF. After the repeated washing and filtration, the resulting solid was dried overnight in a high vacuum, to give 0.4g of hydroxyl group-functionalized MWNT(MWNT-OH).⁴

Grafting of PLLA chains onto the Organo-MWNTs. Before polymerization, the MWNT-OH was dried in a ventilated oven at 70°C overnight. A desired amount of the MWNT-OH was further dried in a round flask under vacuum at 70°C for 3 h. The dried MWNT-OH was then allowed to swell in 100 mL of dry toluene for 1 h at 70°C under nitrogen atmosphere. The hydroxy groups of MWNT-OH were then derivatized into aluminum-alkoxide-active species by reacting with triethylaluminum, AlEt_3 , ($[\text{OH}]/[\text{Al}] = 3$) for an additional hour at 70°C. A given amount of L-lactide was then added under nitrogen atmosphere, and the reaction was allowed to proceed at 70°C for 1~7 days, depending on the reaction conditions. The polymerization reaction was stopped by the addition of diluted HCl.⁵

Measurements. Transmission electron microscopy (TEM) images were obtained by TEM 2000 EX-II instrument (JEOL, Tokyo, Japan) operated at an accelerating voltage of 100 kV. And the amount of PLLA grafted to MWNT was examined by thermogravimetric analysis (TGA) (Q50, TA Instrument). The morphology of the PLLA-g-MWNT-OH hybrid was observed with a scanning electron microscope (SEM, Hitachi S-4300) at an accelerating voltage of 15 kV after pre-coating with a homogenous Pt layer by ion sputter(Hitachi, E-1030).

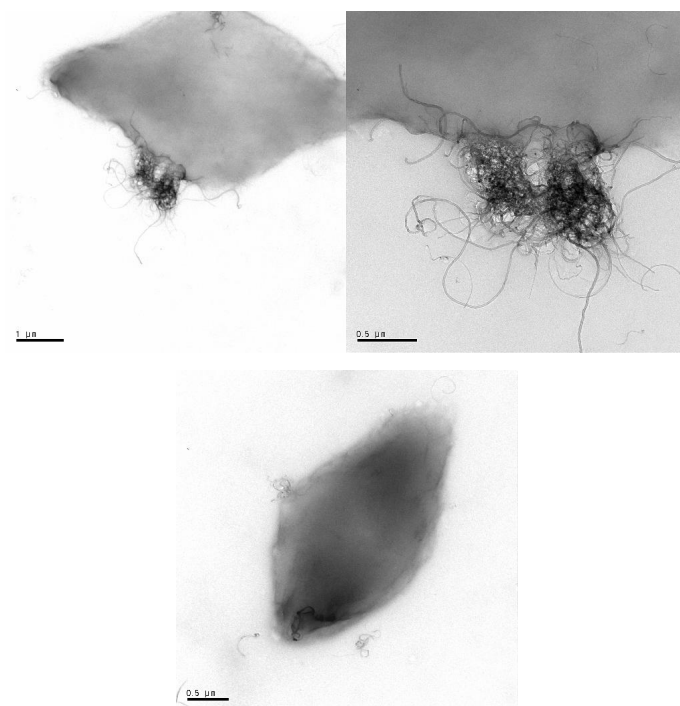


Figure 2. TEM images of the PLLA-g-MWNT-OH (scale bar = 1 μm , 0.5 μm).

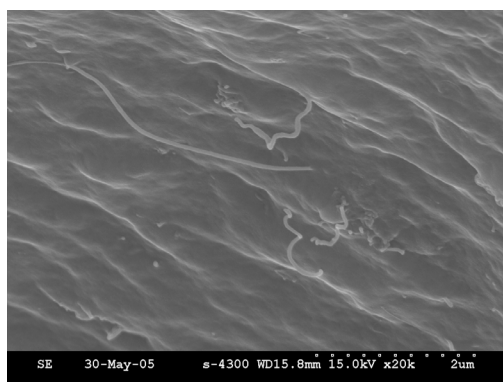


Figure 3. SEM images of the PLLA-g-MWNT-OH (scale bar = 50 nm).

DISCUSSION

The grafting of PLLA chains onto MWNTs has been performed according to a three step synthetic strategy. Aluminum alkoxide are well known for their high efficiency to promote the controlled ring-opening polymerization of L-lactide under mild conditions.

The nanotube dispersion was examined by TEM. The TEM specimen was prepared by depositing a drop of the sample solution onto a carbon-coated copper grid, followed by solvent evaporation. As shown in Figure 2, the PLLA-g-MWNT-OH is apparently well dispersed in the PLLA matrix as well

as in the solvent. The TEM image reveals the nanotube wall stained with PLLA. The nanotubes do not appear shortened significantly despite the reaction involving the severe sonication.

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REFERENCES

1. Alexandre, M.; Dubois, P. *Mater. Sci. Eng.* **2000**, *R28*, 1.
2. Biswas, M.; Ray, S. S. *AdV. Polym. Sci.* **2000**, *155*, 167.
3. Giannelis, E. P. *AdV. Mater.* **1996**, *8*, 29.
4. Qin S. Qin D. Ford W. T. Resasco D. E. Herrera. J. E. *J. Am. Chem. Soc.* **2004**, *126*, 170.
5. Pascal V.; Roberto L.; Eric P.; Michael A.; Philippe D. *J. Am. Chem. Soc.* **2004**, *126*, 9007.