개환중합을 통한 폴리락트산과 탄소나노튜브의 합성

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Synthesis of poly(L-lactide)-*graft*-carbon nanotube via Ring Opening Polymerization

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INTRODUCTION

A number of methods have been attempted for the preparation of polymer/carbon nanotube composites: solution or melt mixing of the carbon nanotubes (CNT) with preformed polymers,[1] electrospinning,[2] *in-situ* polymerization,[3] surfactant-assisted processing of CNTcomposites,[4] and chemical modification of the incorporated CNT.[5]

In the present study, we introduced a new technology to obtain CNT/poly(L-lactide) composites. The interfacial bonding was enhanced through covalent reaction between the polymer chain and the functionalized CNTs to enlarge the applicability of the resulting composites. DMF was selected as the solvent for the ring-opening polymerization because it dissolved both the monomer and the PLLA unbound to the CNT. Moreover it allows a high reaction temperature to make the catalyst highly active. The resulting CNT-*g*-poly(L-lactide) hybrid was characterized by TEM, SEM and TGA.

EXPERIMENTAL

The acid treated MWNTs (MWNT-COOH) was reacted with excess SOCl₂ for 24 h under reflux, and then the residual SOCl₂ was removed by distillation under reduced pressure to yield acyl chloride-functionalized MWNTs (MWNT-COCl). The as produced MWNT-COCl was reacted with excess butane diol at 120℃ for 48h. After washing and filtration, the resulting solid was dried overnight in a vacuum to give the hydroxyl group functionalized MWNTs (MWNT-OH). The resulting MWNT-OH was allowed to swell in 200 ㎖ of dry DMF for 1 h at 140℃. The swollen carboxylic acid-functionalized MWNTs were sonicated in a bath (28 kHz) for 30 min and then was added Tin(II) 2-ethylhexanoate containing solution under a nitrogen atmosphere followed by the sonication in the bath for another 10 min. A pre-determined amount of L-Lactide was then added under nitrogen atmosphere, and the reaction was allowed to proceed at 140℃ for 24 hours. After cooling down to room temperature, the reaction medium was vacuum-filtered through a 0.22㎛ polycarbonate membrane.

RESULT AND DISCUSSION

Figure 1 displays the SEM image of the ring-opening polymerized product after the filtration(PLLA/PLLA-*g*-MWNT-OH). The MWNT-OH was dispersed in PLLA-containing DMF solution and the solution was cast on a flat glass plate. The SEM image of the resulting simple solvent cast composite(PLLA/MWNT-OH) is also displayed in Figure 1 for comparison. As shown in Figure 1a, it is obvious that the PLLA/PLLA-*g*-MWNT-OH composite contained a substantial amount of MWNT-OH well-dispersed in the PLLA matrix. Further more, it can be seen that the MWNT-OH looks embedded in the PLLA matrix (Figure 1b). The PLLA on the surface of MWNT-OH has imparted strong surface charging effects to the MWNT-OH to cause the vagueness of the image. Figures 1c-d show the SEM images of PLLA/MWNT-OH composite with 1 wt% of MWNT-OH. The MWNT-OH was not homogeneously dispersed in the PLLA matrix but a lot of aggregation took place.

More evidences for the PLLA-*g*-MWNT-OH cam be found from the TEM images. Figure 2 shows the TEM images of MWNT-OH and PLLA-*g*-MWNT-OH. The latter was prepared from the PLLA/PLLA-*g*-MWNT-OH by many times of washing with plenty of chloroform under sonication to remove the unbound PLLA completely. In the images of pristine MWNT-OH (Figure 2a), individual tubes separated from each other are obviously discernible, and its high-magnification image (Figure 2b) reveals that the tube wall is clean without any extra phase having different gray tint. In contrast, MWNT-*g*-PLLAs look stained with PLLA, and they are stuck together at the points of intersection.
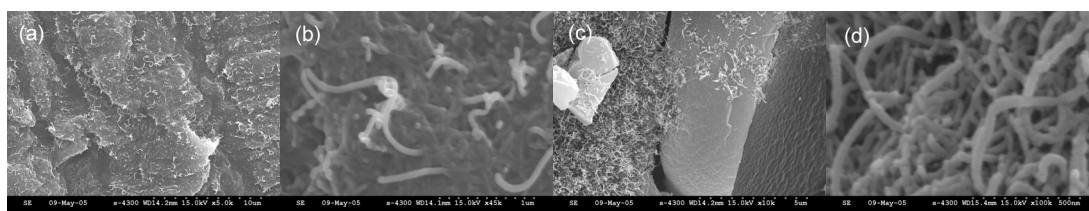

Figure 1 SEM images of (a-b) the PLLA/PLLA-*g*-MWNT-OH composite after the filtration at lower and higher magnifications; (c-d) the solution cast PLLA/MWNT-OH composite at lower and higher magnifications.
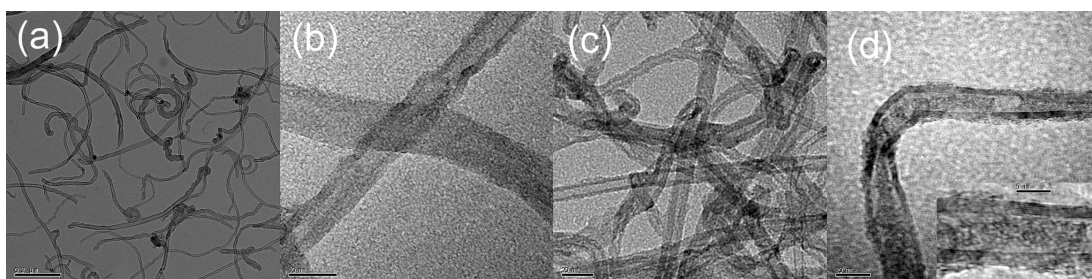
Figure 2 TEM images of (a-b) MWNT-OH at lower and higher magnifications and (c-d)
PLLA-*g*-MWNT-OH hybrid at lower and higher magnifications

The weight fraction of MWNT in the PLLA-*g*-MWNT-OH hybrid was determined from the corresponding TGA scan by thermally decomposing the bound organic substances. As shown in Figure 3, the weight of the PLLA-*g*-MWNT-OH decreased rapidly near 420°C due to the decomposition of the bound organic substances, and only the crude MWNT seemed to be left behind as the temperature approached to 800°C. According to the TGA traces, the thermal stability of the PLLA was dramatically improved by the covalent bonding with the MWNT-OH. The TGA traces also revealed that the MWNT content in the PLLA-*g*-MWNT-OH was approximately 64 wt%.

Therefore it can be concluded that PLLA chains were covalently linked to MWNT-OH by the ring opening polymerization. The simplicity and versatility of this approach will open new avenues for the functionalization and application of the nanocomposites.
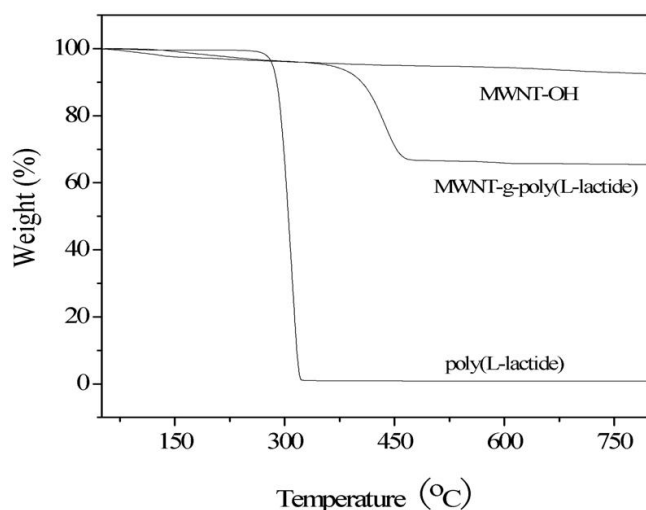

Figure 3 TGA traces (heating rate 20 °C/min in continuous nitrogen flow) of the MWNT-OH, PLLA-*g*-MWNT-OH hybrid and the neat PLLA.

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