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## Poly(L-lactide)/nano-structured carbon composites: Conductivity, thermal properties, crystallization, and biodegradation

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## Abstract

The effects of nano-structured carbon fillers [fullerene  $C_{60}$ , single wall carbon nanotube (SWCNT), carbon nanohorn (CNH), carbon nanoballoon (CNB), and ketjenblack (KB)] and conventional carbon fillers [conductive grade and graphitized carbon black (CB)] on conductivity (resistance), thermal properties, crystallization, and proteinase K-catalyzed enzymatic degradation of poly(L-lactide) [i.e., poly(L-lactic acid) (PLLA)] films were investigated. Even at low filler concentrations such as 1 wt%, the addition of SWCNT effectively decreased the resistivity of PLLA film compared with that of conventional CB, and PLLA–SWCNT film with filler concentration of 10 wt% attained the resistivity lower than 100  $\Omega$  cm. The crystallization of PLLA further decreased the resistivity of films. The addition of carbon fillers, except for  $C_{60}$  and CNB at 5 wt%, lowered the glass transition temperature, whereas the addition of carbon fillers, excluding  $C_{60}$ , elevated softening temperatures, if an appropriate filler concentration was selected. On heating from room temperature, cold crystallization temperature was determined mainly by the molecular weight of PLLA, whereas on cooling from the melt, the carbon fillers, excluding KB, elevated the cold crystallization temperature, reflecting the effectiveness of most of the carbon fillers as nucleating agents. Despite the nucleating effects, the addition of carbon fillers decreased the enthalpy of cold crystallization of PLLA on both heating and cooling. The addition of CNH, CNB, and CB elevated the starting temperature of thermal degradation of PLLA, whereas the addition of SWCNT reduced the thermal stability. Furthermore, the addition of  $C_{60}$ and SWCNT enhanced the enzymatic degradation of PLLA, whereas the addition of KB and CNB disturbed the enzymatic degradation of PLLA. The reasons for the effects of carbon fillers on the physical properties, crystallization, and enzymatic degradation of PLLA films are discussed. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Poly(lactic acid); Polylactide; Nano-structured carbons

## 1. Introduction

Biomass-derived poly(L-lactide), i.e., poly(L-lactic acid) (PLLA) has been intensively explored because it is biodegradable, compostable, producible from renewable resources, and nontoxic to the human body and the environment. The improvement of physical properties of PLLA, such as mechanical, thermal, and electrical ones, is a matter of concern, especially when used in industrial and commodity applications [1-12]. For

\* Corresponding author. *E-mail address:* tsuji@eco.tut.ac.jp (H. Tsuji). improvement of these properties, the addition of various types of fillers is commercially advantageous, because the physical properties are readily manipulated by the type and concentration of fillers. Talc and montmorillonite are representative cost-effective fillers for PLLA to improve crystallinity, thermal stability, and mechanical properties [13–19].

In our previous study, we investigated the nucleating effects of fullerene  $C_{60}$  and poly(D-lactide), i.e., poly(D-lactic acid) (PDLA) (or the stereocomplex crystallites formed upon addition of PDLA to PLLA) on the crystallization behavior of PLLA [19,20]. It was found that the acceleration effects of fillers on the overall PLLA crystallization during cooling from the melt decreased in the following order: PDLA >

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