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Thermal degradation of novel exfoliated PLLA/LDH nanocomposites

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Abstract. In this article, we report the fabrication of novel poly(L-lactide) (PLLA) nanocomposites based on PLLA and magnesium-aluminium layered double hydroxides (MgAl-LDH) which were mixed the polylactide with carboxyl end group (PLA-COOH) in acetone . Both the X-ray diffraction data and transmission electron microscopy images of the PLLA/LDH nanocomposites indicate that most of the LDH layers were disorderly exfoliated into the PLLA matrix. The thermal degradation behaviors of PLLA and its nanocomposites were studied using thermal gravimetric analysis (TGA) under nitrogen atmosphere at heating rates from 5 to 40 °C/min. The TGA profiles of the PLLA/LDH nanocomposites show less thermal stability than that of neat PLLA due to the presence of Mg and Al which has a drastic influence on thermal stability of PLLA. The activation energy of PLLA, 1 wt% and 3 wt% PLLA/LDH nanocomposites were 158, 140 and 130 kJ/mol, respectively.

Introduction

In recent years, polymer/clay nanocomposites have attracted considerable interest owing to their unique physico-chemical and mechanical properties that are unattainable from the neat polymers or conventional composites [1-3]. The enhancement of these properties is significantly predominated by the dispersion degree of clay into the polymer and the strong interaction between the polymer and clay. Although the preparation and characterization of various polymer/montmorillonite (MMT) nanocomposites have extensively reported in the literature [1], there is only little literature on polymer/layered double hydroxide (LDH) nanocomposites because of the strong interlayer electrostatic interactions and small gallery space of LDH [4]. Nevertheless, the highly tunable characteristics of the LDH structures are different from those of the MMT, which can be considered as a new promising class of inorganic filler for the preparation of novel nanocomposites.

The biodegradable polymer, polylactide (PLA), has been extensively used for the fabrication of PLA/MMT nanocomposites by solution intercalation [5] or melt compounding [6].The physical properties of these PLA/MMT nanocomposites show significant enhancement compared to that of pure PLA. Nevertheless, there is little research reported for the PLA/LDH nanocomposites. The aim of present study is to prepare the PLLA/LDH nanocomposites via solution intercalation and to investigate the influences of LDH on thermal properties of PLLA by thermogravimetry analysis (TGA).

Experimental

Materials and sample preparation. Poly(l-lactide) (PLLA), Poly(DL-lactide) with carboxyl end group (PLA-COOH), $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and sodium hydroxide were used without further purification. Magnesium-aluminum layered double hydroxides (MgAl-LDH) were prepared by the co-precipitation method [7]. The aqueous solution containing $Mg(NO_3)_2 \cdot 6H_2O$ (0.096 mol) and $Al(NO_3)_3 \cdot 9H_2O$ (0.048 mol) was vigorously stirred at 60°C for 16 h and adjusted to pH ~ 10 with 2N NaOH aqueous solution. The white slurry was filtered and washed by deionized water. In order to avoid the pollution of carbonate, all of experimental processes proceeded under the nitrogen atmosphere. For the preparation of organically modified layered double hydroxides (P-LDH), 0.5 g MgAl-LDH and 0.5 g PLA-COOH were prepared by dissolving in 50 and 100 ml acetone,

respectively. These solutions were mixed and refluxed at 70°C for 48 h under nitrogen atmosphere. The obtained slurry was filtered and washed by acetone. The product was finally obtained by lyophilizing in cacuum. The tetrahydrofuran (THF) suspension (20 ml) of P-LDH was mixed with 30 ml of a THF solution of PLLA for the preparation of 1 wt% and 3 wt% PLLA/LDH nanocomposites. In the preparation of PLLA/LDH nanocomposites films, each THF solution of the sample was stirred at room temperature for 24 h and then evaporated in a glass Petri dish for 48 h.

Characterization. The wide angle X-ray diffraction (WAXD) measurements were performed using a Rigaku III diffractometer equipped with Ni-filtered Cu Kα radiation. The transmission electron microscopy (TEM) images were obtained on a JEOL JEM-1200 CX II transmission electron microanalyzer with an accelerating voltage of 120 KV. The specimen was ultramicrotomed with a diamond knife to give a thickness of about 100 nm silices, and silices were collected on carbon-coated copper grid. For thermal stability and thermal degradation behavior of PLLA and its nanocomposites, TGA examinations of specimens were performed on a Perkin-Elmer thermogravimetric/differential thermal analyzer (TG/DTA) 6300. Mg and Al analyses were performed on Jarrell-Ash ICAP 9000 Inductively Coupled Plasma-Mass Spectrometer.

Results and Discussion

Fig. 1A reveals the X-ray diffraction patterns of MgAl-LDH and P-LDH. The interlayer distance of the MgAl-LDH is measured to be 7.89 Å from the d_{003} diffraction peak at 2θ=11.2° (Fig. 1A, trace a). As a result of ion exchange between the interlayer anion and PLA-COOH, the X-ray data of P-LDH shifts into a smaller angle at 2θ=6.23°, which corresponds to an interlayer distance of 14.19 Å (trace b in Fig. 1A). The X-ray diffraction patterns of PLLA/LDH nanocomposites are also shown in Fig. 1A. Both X-ray diffraction data of 1 wt% and 3 wt% PLLA/LDH nanocomposites revealed no d_{003}-reflection peak in the relevant region, indicating the presence of interlayer distances at least larger than 48 Å or no regular periodicity. This finding could suggest that the hydrophobic interactions between the PLA-COOH chains and PLLA matrix might completely destroy the layered structure. Although XRD measurement is a powerful and essential technique to estimate the extent of intercalation and/or exfoliation of layered material, TEM instrument can be used to visually examine the dispersal behavior of the LDH layers in the PLLA matrix. Fig. 1B displays a TEM image of 3 wt% PLLA/LDH nanocomposites. From the TEM result, it is clear that the stacks of LDH layers are disorderly dispersed in the PLLA matrix. Therefore, these results are strongly supported that the order of LDH layers lose their ordered stacking structure and are randomly distributed in PLLA matrix.

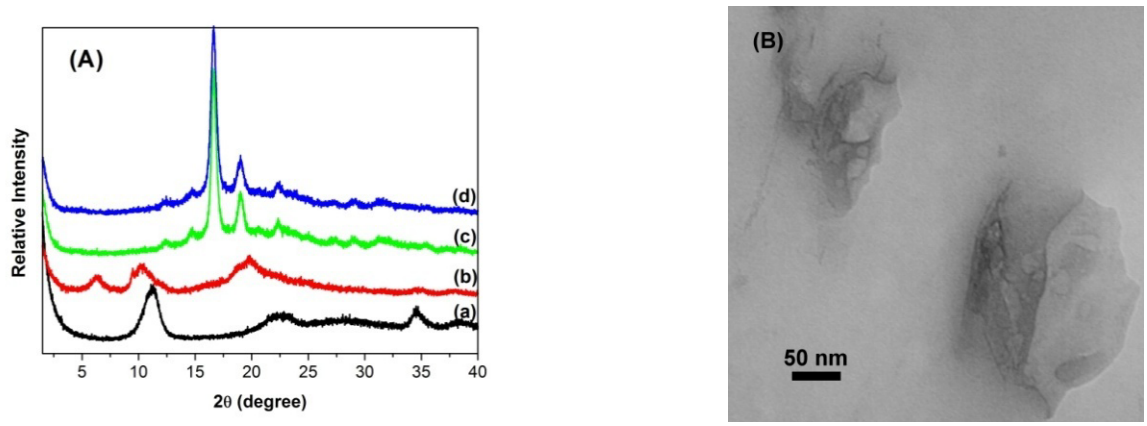

Figure 1. (A) XRD patterns of (a) MgAl-LDH, (b) P-LDH, (c) 1 wt% PLLA/LDH, and (d) 3 wt% PLLA/LDH in the range of 2θ=1.5°-40°. (B) TEM image of 3 wt% PLLA/LDH nanocomposites.

In order to investigate the influence of MgAl-LDH on the thermal degradation behavior of PLLA, TGA/DTA analysis was employed to identify the nonisothermal degradation of PLLA and PLLA/LDH nanocomposites. Fig. 2A illustrates the TGA profiles of weight loss as a function of temperature for PLLA and PLLA/LDH nanocomposites at a heating rate of 10°C/min. All results of

PLLA/LDH nanocomposites show less thermal stabilities than neat PLLA. The decomposition temperature at 50% weight loss for pure PLLA, 1 wt% PLLA/LDH and 3 wt% PLLA/LDH are 351, 328 and 312 °C, respectively. The results indicate the decomposition temperature of PLLA decreases as the amount of P-LDH increases. It's necessary to point out that these data are in contrast with the previous investigations for polymer/LDH nanocomposites [8,9] which reveal the improvement of the thermal stability for those polymers by adding the LDH.

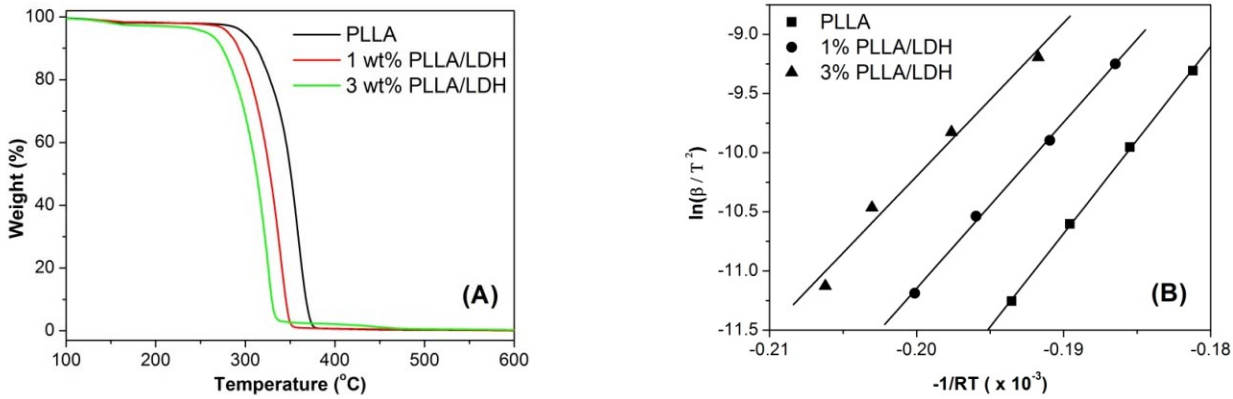

Figure 2. (A) TGA curves of PLLA, 1 wt% PLLA/LDH, and 3 wt% PLLA/LDH samples at 10°C/min in a constant nitrogen flow (100 ml/min). (B) Activation energy plots of $\ln(\beta/T^2)$ versus -1/RT for PLLA and PLLA/LDH nanocomposites.

For further investigation of the influence of LDH on the thermal degradation of PLLA/LDH nanocomposites, the activation energies (E_a) of thermal degradation for the PLLA/LDH nanocomposites are estimated by the TGA/DTA data. The activation energy of thermal degradation could provides the evaluation of thermal stability of PLLA/LDH nanocomposites. Therefore, the plots of $\ln(\beta/T_2)$ versus -1/RT for PLLA and PLLA/LDH nanocomposites are presented in Fig. 2B. The E_a values determined by Kissinger method [10] would be estimated from the slopes of the straight lines in Fig. 2B and summarized in Table 1. The calculated E_a of PLLA, 1 wt% PLLA/LDH and 3 wt% PLLA/LDH are 158.04, 140.50 and 129.52 kJ/mol, respectively. These calculated results reveal that the E_a of thermal degradation of the PLLA matrix decrease as the MgAl-LDH contents increase. From these results, the thermal stability of the samples would be in the following order: PLLA > 1 wt% PLLA/LDH > 3 wt% PLLA/LDH. Therefore, a possible explanation for the reduction in the E_a values needs to be reached. Actually, Cam et al. [11] had proposed a theory that the Al could cause significant thermal degradative effect of PLLA. Fan et al. [12] had studied the thermal degradation behavior of the PLLA/MgO composites and their results revealed that MgO could act as an effective catalyst for reducing the degradation temperature of PLLA. Therefore, the contents of Mg and Al residues in PLLA matrix were further examined by ICP and their corresponding results are also listed in Table 1. These data can provide sufficient evidence to prove that the thermal stability of PLLA decreases with increasing the amounts of Mg and Al. The main reason for the decreasing thermal stability might be caused by the presence of Mg and Al in PLLA that can accelerate the depolymerization and/or inter- and intra-molecular transesterification reactions of the PLLA [11].

Table 1 The degradation activation energies (E_a) obtained from the Kissinger method.

Sample code	E_a [kJ/mol]	$R^{(1)}$	$Mg^{(2)}$ [wt%]	$Al^{(2)}$ [wt%]
PLLA	158.04	0.9998	-	-
1% PLLA/LDH	140.50	0.9993	0.020	0.027
3% PLLA/LDH	129.52	0.9902	0.137	0.100

(1) R: correlation coefficient.
(2) Mg and Al ratio were obtained from ICP experiment.

Summary

From XRD and TEM results, the disorderly dispersed PLLA/LDH nanocomposites have been successfully prepared by the incorporation of PLA-COOH modified MgAl-LDH into PLLA matrix. Thermogravimetric studies indicated that thermal degradation temperature of PLLA/LDH nanocomposites shift to lower temperature ranges compared to that of neat PLLA. Degradation kinetics of PLLA and its nanocomposites were investigated by TGA/DTA and the results showed E_a values decrease with increasing the content of Mg and Al. Moreover, this phenomenon may be attributed to the presence of Mg and Al that catalyse the depolymerization and/or inter- and intra-molecular transesterification reactions of PLLA.

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