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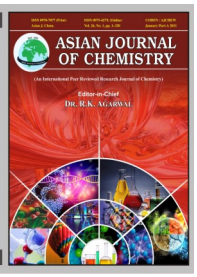

Isothermal Crystallization Behavior of Poly(L-lactic acid)/Organo-Montmorillonite Composites

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In this research, organo-montmorillonite (OMMT) was synthesized by ion exchange technology, Then the poly(L-lactic acid)(PLLA)/OMMT composites were fabricated using melt blending and hot-press forming. The isothermal crystallization behavior of PLLA/OMMT composites was investigated in detail and isothermal crystllization behavior was affected by crystallization temperature and organo-montmorillonite content. Compared to the neat poly(L-lactic acid), the half-time of poly(L-lactic acid) with 5 % organo-montmorillonite decreases from 2991.5s to 327s. and the kinetic of isothermal crystallization of PLLA/OMMT was described by Avrami theory and the results showed that PLLA/OMMT composite had complicated nucleation mechanism.

Keywords: Montmorillonite, Crystallization time, Poly(L-lactic acid), Crystallization kinetic.

INTRODUCTION

Montmorillonite (MMT), as a very important layer silicate, is widely used in all field such as materials[1-2], geosorbents[3], chemistry[4-5], waster repositories[6], *etc*. Especially, the most important application of montmorillonite is additive of polymer in recent years[7-8]. Montmorillonite can improve the impact resistance, dimensional stability, crystallization properties of polymer, for example, Zhang *et al.*[9] reported the preparation and properties of polyester-organophilic montmorillonite intercalated hybrid. The result of this investigation showed that when the content of organophilic montmorillonite was between 2 and 5 %, the tensile strength, impact strength, heat resistance and swelling resistance of the hybrid were obviously enhanced.The nonisothermal crystallization kinetics of polyoxymethylene/organic-montmorillonite (POM/organ-MMT) composites was investigated[10]. The difference in the values of the exponent 'n' between polyoxymethylene and POM/MMT composites suggested that nonisothermal crystallization of POM/organ-MMT nanocomposites corresponds to a tridimensional growth with heterogeneous nucleation. And the crystallization rate of POM/organ-MMT nanocomposite is faster than that of neat POM at a given cooling rate. These results further indicated that the addition of montmorillonite may accelerate the overall non-isothermal crystallization process of polyoxymethylene.

However, the montmorillonite as an additive of polymer usually modified by chemical method and compatibility ability is improved between polymer and modified montmorillonite with organic group. Thus, it is very necessary to modify montmorillonite to make it competitive with advanced additive.

Poly(L-lactic acid)(PLLA) has been successfully applied in many field of production and life and poly(L-lactic acid), either research field or production field, holds a leading position in biodegradation polymer. However, poly(L-lactic acid) itself has some disadvantage to limit its application, slow crystallization rate is the most serious defect. Thus, many researchers try their best to improve the crystallization rate to further widen the application of poly(L-lactic acid)[11,12]. Montmorillonite (MMT) is often used the nucleating agent of poly(L-lactic acid) to improve the crystallization rate[7,13]. However, many research work need to be done to futher know the role of MMT to improve the crystallization of poly(L-lactic acid). Thus, first MMT is modified by ion exchange technology and then the PLLA/OMMT composites were prepraed. The isothermal crystallization behavior of PLLA/OMMT was investigated.

EXPERIMENTAL

Poly(L-lactic acid) PLLA (3051D) was purchased from Nature Works LLC, USA. Montmorillonit was procured from Mianyang Rongshen Chemical Reagents Company (Sichuan Province, China), Hexadecyl trimethyl ammonium bromide, silver nitrate were purchased from Beijing Chemical Reagents Company (Beijing, Chian).

Preparation of organo-montmorillonite(OMMT): Montmorillonite and water were mixed and the mixture was heated up to 80 °C with stirring, the hexadecyl trimethyl ammonium bromide was added slowly into the mixture and the mixture was stirred at 80 °C for 4 h, Reaction mixture was washed by water not to detect Cl^-. the organo-montmorillonite was dried in vacuum at 65 °C.

Preparation of PLLA/OMMT: Blending of poly(L-lactic acid) and dried organo-montmorillonite was performed on a counter-rotating mixer with a rotation speed of 32 rpm for 5 min, then at 64 rpm for 5 min. The processing temperature was set at 185 °C. Then, the mixture were hot pressed at 180 °C under 20 MPa for 3 min and cool pressed at room temperature under 20 MPa for 10 min.

Characterization: Wide angle X-ray diffraction (WAXD): WAXD experiments were performed on a diffractometer (D/MAX2550, Rigaku, Japan) using CuK_α radiation (wavelength, 1.54 Å) at room temperature in the range of 2θ = 5-50º with scanning rate of 2 º/min.

Depolarized-light intensity measurement: Isothermal crystallization behavior of poly(L-lactic acid) was investigated by GJY-IIIoptical depolarizer in the region from 100 to 120 ºC. The electronic signals transformed from the measured optical depolarizer were amplified and then recorded.

RESULTS AND DISCUSSION

XRD of organo-montmorillonite: Fig.1 shows XRD of organo-montmorillonite and the date of Na-MMT and organo-montmorillonite was listed in Table-1. As shown in Fig.1 and Table-1, the spacing of layers and diffraction angle of MMT significantly change after modifing MMT using hexadecyl trimethyl ammonium bromide. Compared to Na-MMT, The diffraction angle of the (001) plane of organo-montmorillonite shifts from 7.15 to 5.38 and the spacing of layers also increases from 1.27 to 2.27.

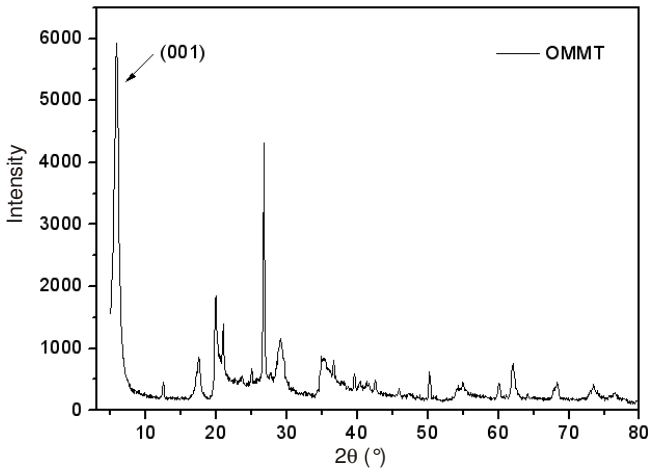


Fig.1. XRD of organo-montmorillonite

TABLE-1
XRD DATE OF MMT

Sample	2θ (º)	d_{001} (nm)
Na-MMT	7.15	1.27
OMMT	5.38	2.27

Isothermal crystallization of PLLA/OMMT composites: Isothermal crystallization of polymer is very important to widen application of polymer. Thus, many researchers investigated the isothermal crystallization of polymer composites[14,15], especially, effect of additive on isothermal crystallization of polymer. In this paper, isothermal crystallization behavior is investigated by using depolarized-light intensity technique[16]. Fig. 2 shows the effect of the organo-montmorillonite content and crystallization temperature (T_c) against the half time of overall poly(L-lactic acid) crystallization $t_{1/2}$. With increasing of crystallization tenperature, the $t_{1/2}$ becomes shorter firstly, then increases. However, it is clear that there are not similar minimun value at some same temperature, which indicates that organo-montmorillonite affects the crystallization behavior of poly(L-lactic acid). In addition, the content of organo-montmorillonite also affect the crystallization of poly(L-lactic acid), the $t_{1/2}$ becomes shorter with increasing of content of organo-montmorillonite. To compare with the neat poly(L-lactic acid), $t_{1/2}$ decreases from 2991.5s to minimum value 327s, with 5 % organo-montmorillonite contents at 105 °C. When organo-montmorillonite content is further increased, the $t_{1/2}$ starts to become longer.

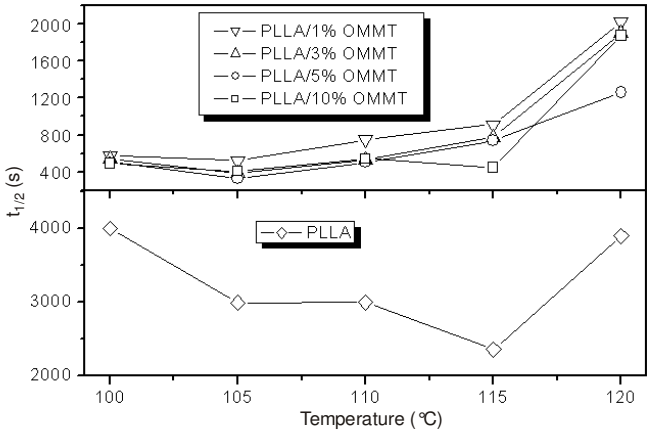


Fig. 2. $T_{1/2}$ of poly(L-lactic acid) and PLLA/OMMT composites with the crystallization temperature T_c

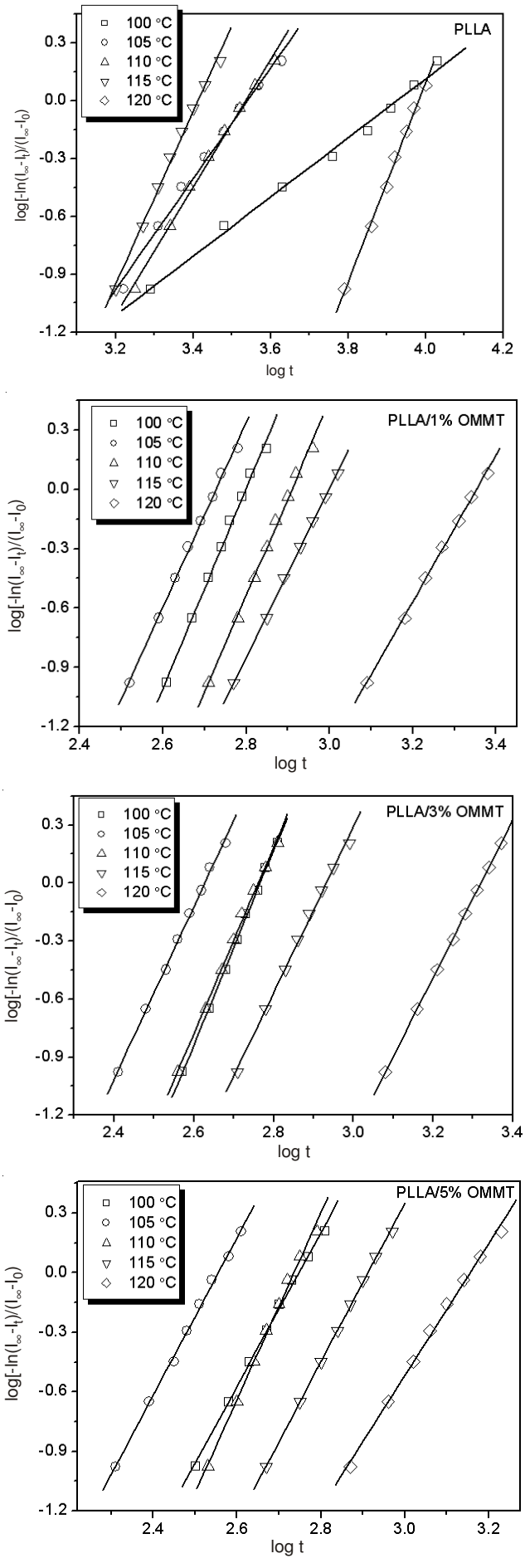
Avrami equation is widely used to describe the kinetic of isothermal crystallization of polymer and isothermal crystallization process can be analysed by the following equation[17]:

$$1-\frac{X_c}{100}=\exp(-kt^n) \quad (1)$$

where k is the crystallization rate constant (min^{-1}) and n value is the Avrami exponent. $X_c(t)$ represents the percentage of relative crystallization after time *t*. Eqn (1) can be transformed to eqn. (2).

$$\lg[-\mathrm{In}(\frac{X_t}{100})]=\lg k+n\lg t \quad (2)$$

In this paper, we used the relative light intensity (I_r) as X_c in eqn (2). Fig. 3 shows the avrami plots of poly(L-lactic acid) and PLLA/OMMT composites, the relationship of log[-ln(1-Xt)] *versus* logt is linear. Obtained the kinetic parameters 'n' and 'k' values of neat poly(L-lactic acid) and PLLA/OMMT composites are listed in Table-2. Generally, 'n' is 4 in homogeneous nucleation system and 3 in heterogeneous nucleation system.



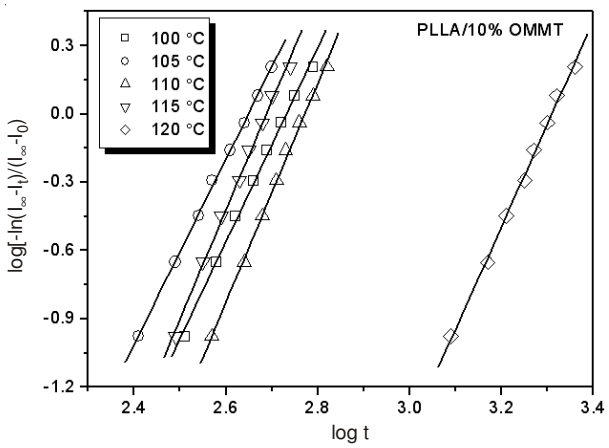


Fig. 3. Avrami plots for poly(L-lactic acid) and PLLA/OMMT composites at different temperature

TABLE-2
ISOTHERMAL CRYSTALLIZATION PARAMETERS OF PLLA AND PLLA/OMMT COMPOSITES

Sample	T_c (°C)	n	log K
PLLA	100	1.5	-6.03
	105	2.9	-10.17
	110	3.3	-11.69
	115	4.4	-15.27
	120	5.1	-20.61
PLLA/1 % OMMT	100	5.0	-14.15
	105	4.6	-12.68
	110	4.9	-14.26
	115	4.3	-12.79
	120	3.7	-12.41
PLLA/3 % OMMT	100	5.0	-13.90
	105	4.5	-11.70
	110	4.8	-13.33
	115	4.3	-12.60
	120	4.1	-13.55
PLLA/5 % OMMT	100	3.8	-10.64
	105	3.9	-10.14
	110	4.7	-12.84
	115	4.0	-11.66
	120	3.3	-10.50
PLLA/10 % OMMT	100	4.2	-11.65
	105	4.1	-10.79
	110	4.8	-13.37
	115	4.7	-12.87
	120	4.5	-14.94

From Table-1 we can see that the 'n' values of pure poly(L-lactic acid) is between 1.5 to 5.1, which indicates that the crystallization of the neat poly(L-lactic acid) is affected by crystallization temperature. And for PLLA/OMMT composites, the 'n' values range between 3.3 and 5 as the increasing T_c representing that PLLA/OMMT composite not only take a heterogeneous nucleation process followed by a three-dimensional crystal growth but also have other complicated nucleation mechanism. The k values have a similar trend with the $t_{1/2}$ values.

Conclusion

Organo-montmorillonite was synthesized and characterized by XRD. Isothermal crystallization behavior of PLLA/OMMT was investigated and the results showed that isothermal

crystllization behavior was affected by crystallization temperature and OMMT content. The half-time of poly(L-lactic acid) with 5 % OMMT decreases from 2991.5s to 327s. And PLLA/OMMT composite had very complicated nucleation mechanism.

ACKNOWLEDGEMENTS

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