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Isothermal Crystallization Behavior of Poly (L-lactic acid)/ Surface-grafted Silica Nanocomposites

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Abstract: The Poly(L-lactic acid)(PLLA)/surface-grafting silica(g-SiO_2) nanocomposites were prepared by melt blending. The isothermal crystallization behavior of PLLA/g-SiO_2 nanocomposites with different content of g-SiO_2 was investigated by optical depolarizer. In isothermal crystallization from melt, the induction periods and half times for overall PLLA crystallization ($95℃ \leq T_c \leq 120℃$) were affected by the crystallization temperature and the content of g-SiO_2 in nanocomposites. The results showed that g-SiO_2 as a kind of heterogeneous nucleating agent can reduce induction periods and half times for overall PLLA crystallization. The thermal properties of PLLA/g-SiO_2 samples were also investigated by differential scanning calorimetry (DSC), The results showed that the crystalline degree of PLLA was improved as the presence of g-SiO_2.

1. Introduction

Poly(L-lactic acid)(PLLA), as a kind of biodegradable polymer that get rid of the dependence of petroleum recourses, has gained considerable momentum in recent years [1-5] due to its properties such as biodegradability, non-toxic to the environment, etc [6]. However, the application of PLLA was limited because of its brittleness and especially low crystallization [7]. Thus, it is necessary to improve PLLA to make it fully competitive with commercial thermoplastics. To improve crystallization and blending have been used to modify PLLA. Inorganic fillers are often introduced into PLLA as nucleating agents to increase crystallization rate, some works have given us many helpful references [8-10]. For example, Pluta et al. [8] studied the crystallization behavior and the morphology of neat PLA and PLA/OMMT nanocomposites. His work has shown that clay particles act as nucleating agent for the crystallization of the matrix PLA, but he didn't report the overall crystallization rate and spherulite growth rate of PLA before and after nanocomposites preparation. Nam et al. [9] have described the detailed crystallization behavior and morphology of pure PLA and PLA/C_{18}-MMT nanocomposite, including overall crystallization rate, crystallization kinetics and spherulitic texture of PLA. Krikorian and Pochan [10] amply investigated the crystallization behavior of organoclay reinforced PLLA nanocomposites. Their research was base on two types of organoclay with different extent of compatibility with PLLA. The bulk kinetics studies and radial spherulite growth rates indicated that when a high degree of filler-polymer matrix compatibility is present, nucleation properties of the organoclay are low relative to the less compatible organoclay. Their works are convincing and worth reference, but further investigation should be carried out because it is well known that 10% or 15% of nano-filler is too high to nanocomposites.

PLLA nanocomposites with SiO_2 have been reported[12-16], Linbo Wu et al[12-13] reported PLLA/SiO_2 nanocomposites were prepared via in situ melt polycondensation of L--lactic acid in the presence of acidic silica sol. The SiO_2 nanoparticles acted as nucleation agents in the PLLA matrix and enhanced its nucleation rate and overall crystallization rate, especially at high crystallization temperatures. However, their research ignored the effect of SiO_2 content to crystallization. Thus, in this paper, in order to improve the compatibility and adhesion between SiO_2 and PLLA matrix, the SiO_2 were surface-grafted with *L*-lactic acid oligomer. And the isothermal crystallization behavior of PLLA/surface-grafting silica(g-SiO_2) nanocomposites with different content of g-SiO_2 has been investigated in detail. Furthermore, the influence of the content of g-SiO_2 on the crystallization rate and degree of crystallinity of PLLA/g-SiO_2 nano-composites was investigated.

2. Experimental Section

2.1 Materials

Poly(L-lactic acid) (PLLA) (M_w=1.95×10^5) was purchased from Zhejiang Hisun Group. (China). g-SiO_2 were supplied by Shanghai university.

2.2 Preparation of PLLA/ g-SiO_2 nanocomposites

PLLA and g-SiO_2 were dried over night at 45℃ under vacuum respectively to remove residual water. Blending of PLLA and g-SiO2 was performed on a counter-rotating mixer with a rotation speed of 32 rpm for 4min, then at 64 rpm for 4 min. The processing temperature was set at 180℃. The composites with various amounts (1, 3, 9%) of g-SiO_2 nanoparticles were prepared. Products were hot pressed at 180℃ under 10 MPa for 3 min to prepare sheets. The sheets were then cooled down by being compressed at room temperature under 10 MPa for 15 min.

2.3 Characterization

Depolarized-light intensity measurement: The overall isothermal crystallization behavior of PLLA was investigated by GJY-ⅢIoptical depolarizer in the region from 100℃ to 120℃. The electronic signals transformed from the measured optical depolarizer were amplified and then recorded on the Recording and Data Acquisition for further analyzing.

Differential scanning calorimeter: DSC 200 PC (Netzsch, Germany) was used to measure the equilibrium melting temperature (T_m^0). The sample was heated to 190℃ and maintained at that temperature for 5 min to make sure that the polymer crystals were melted completely. Then the sample was quenched to the crystallization temperature T_c (110℃) by liquid nitrogen, held at that temperature for at least 30 min to ensure complete crystallization. At last, the sample was heated at the heating rate of 20℃/min.

3. Results and discussion

3.1 Overall isothermal crystallization behavior

Traditionally, isothermal crystallization behavior can be investigated by using depolarized-light intensity [15, 16] technique as the transmitted light intensity (I) increases with the increasing of crystallinity and finally levels off when crystallization completes. In our research, we used the relative light intensity (I_r) defined by the following equation as an index of crystallinity:

$$I_r(\%) = 100 \times \frac{(I_t - I_0)}{(I_\infty - I_0)} \quad (1)$$

where I_t and I_0 are the I values at $t_c = t$ and 0, respectively, I_∞ is the I value when crystallization completes. Fig.1 shows the effect of the g-SiO_2 content and the crystallization temperature (T_c) against the induction period t_i and the crystallization rate ($1/t_{1/2}$). With the increasing of crystallization temperature, t_i become shorter due to the enhancement of the macromolecule segment active ability, and t_i has the maximum value when crystallization temperature is 105 ºC, However, t_i become longer with further increasing of crystallization temperature, which result from the formation of spherulite restricted by excessive macromolecule segment activity. The t_i peak of PLLA/g-SiO_2 shift toward lower T_c, which indicate that g-SiO_2 can serve as a good heterogeneous nucleating agent for the crystallization of PLLA in the composites. At same time, the content of g-SiO_2 has great impact of induction period. The t_i decrease by adding more content of g-SiO_2, which confirm again that g-SiO_2 has good heterogeneous nucleation effect. Figure.1 also shows the trend of crystallization rate ($1/t_{1/2}$) with different T_c and g-SiO_2 content. The crystallization rate increase with the increasing content of g-SiO_2 which also can attribute to the heterogeneous nucleation effect of g-SiO_2. However, the crystallization rate of PLLA/g-SiO_2 composites with above 3%g-SiO_2 has the maximum value when crystallization temperature is 110℃, which is different from the induction period.

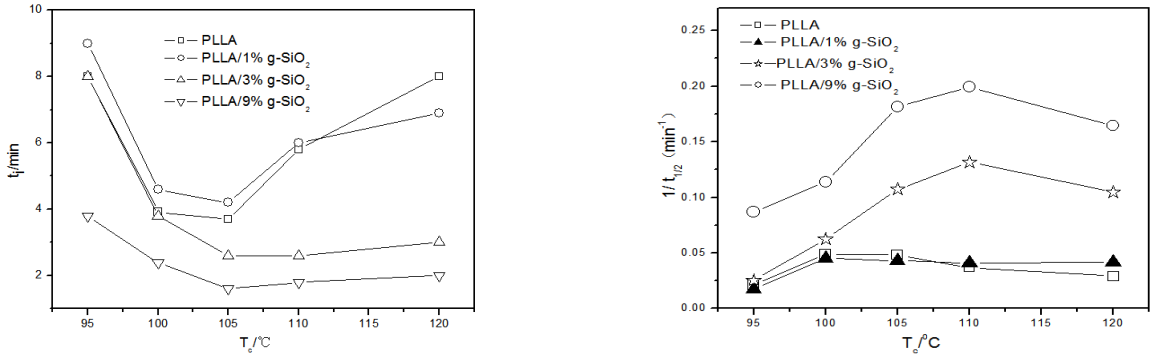

Fig.1 Induction periods (t_i) and crystallization rate ($1/t_{1/2}$) for PLLA/ g-SiO_2 composites with different g-SiO_2 content and crystallization temperature

3.2 Crystallization thermodynamics

The crystallization thermodynamics parameters of neat PLLA and PLLA/g-SiO_2 nanocomposites are listed in Table 1. These samples were measured by DSC after 30min isothermal crystallization at 110℃. By considering ΔH_m^*, melting enthalpy of 100% crystalline PLLA, as 93.7J/g [17], we have estimated the value of crystalline degree χ_c of PLLA in different systems. χ_c of composites should based on the equation:

$$\chi_c = \frac{\Delta H_m}{(1-\phi)\Delta H_m^*} \times 100\% \quad (2)$$

where ϕ is the weight fraction of filler in nanocomposite and ΔH_m is the heat of fusion.

According to the data listed in Table 1, It is clear that g-SiO_2 nanoparticles can serve as a nucleating agent for the crystallization of PLLA in the composites. Compared to the neat PLLA, the crystalline degree χ_c of PLLA matrix increases above 3% g-SiO_2 content. The crystallization temperature (T_c) and the melting temperature (T_m) seem to be independent of loading of g-SiO_2 particles.

Table 1 Thermal parameters of PLLA and PLLA/ g-SiO_2 nanocomposites

Sample		T_c (℃)	T_m (℃)	△ H_f (J/g)	χ_c (%)
PLLA		119.57	155.37	16.79	18.05
PLLA/g-SiO_2	1wt%	127.05	152.16	9.963	10.71
	3wt%	127.37	153.13	18.95	20.38
	9wt%	119.39	152.44	22.19	23.86

4. Conclusions

Investigations on the isothermal crystallization behavior were carried out on the intercalated PLLA nanocomposites prepared by melting blend. The results showed that the g-SiO_2 as a kind of heterogeneous nucleation agent can reduce t_i and $t_{1/2}$. And the crystalline degree of PLLA matrix increases above 3% g-SiO_2 content.

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