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Study on the nonisothermal crystallization behaviorof polyvinyl alcohol/montmorillonite composite by DSC analysis

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Polyvinyl alcohol (PVA)/montmorillonite (MMT) composite films were prepared by a solution-casting technique. The nonisothermal crystallization behavior of PVA and PVA//MMT composite have been investigated by differential scanning calorimetry (DSC). It has been found that the uniformly dispersed MMT in the matrix have a great influence on the crystallization behavior of PVA. The Jeziorny method has been employed to analyze the DSC data. The results show that the Jeziorny method can describe this system very well. Comparing with the PVA, the PVA//MMT composite has a higher crystallinity X_t, shorter semicrystallization time $t_{1/2}$ and higher crystallization rate constant Z_c. It can be concluded that MMT acted as an effective nucleating agent and had an effect on the growth of crystallites in the crystallization process of the PVAmatrix.

Keywords*:*polyvinyl alcohol; Montmorillonite; crystallization behavior; DSC analysis

INTRODUCTION

It is well known that montmorillonite(MMT), a kind of inexpensive natural layered silicate, has been widely used to prepare polymer/layered silicate nanocomposites[1-2]. These composites have excellent overall properties and a low gas permeability. Major preparation methods of the polymer nanocomposites include in situ polymerization and the direct blending method (including polymer melt, solution and emulsion blending). In recent years, more and more researchers are interested in direct blending because it is the most direct, most costefficient method and is benign for the environment [3-6].

As we know, polyvinyl alcohol (PVA) can dissolve in hot water and there are many hydroxyls existing on its molecular chains. So, it is possible that MMT may be dispersed into the material and has good adhesion to the PVA matrix by simple blending. Furthermore, PVA is a semicrystalline polymer in which high physical interaction exists between the polymer chains, due to hydrogen bonding between the hydroxyl groups.

MMT may affect both the crystallinity and the physical network of PVA, causing variations in both the thermodynamic and kinetic characteristics of crystallization. But studies of the effects of MMT on the crystallization of PVA have not been reported.

In this work, PVA/MMT composite films have been prepared by the solution-casting method. The nonisothermal crystallization behavior of the PVA matrix have been investigated by differential scanning calorimetry(DSC) analysis. The nucleation function of MMT has been observed for the crystallization process of the polymer matrix.

EXPERIMENTAL

Materials

The Polyvinyl alcohol, supplied by Chang Chun Petrochemical Co. Ltd. was 99.5% hydrolyzed. The MMT was provided by the Aldrich Corporation and the organics treated by octadecylamine before use.

Sample Preparation

PVA grains were fully dissolved in deionized water by stirring at 95°C. MMT solution was added, this was dispersed in water for about 30 min in an ultrasonic bath at 90°C. The MMT content of PVA was in wt%. The blend was uniformly mixed by strong stiring and placed in an oven for solvent evaporation at 70°C for about 24 h. Then, the blend solution was ready for film preparation.

The PVA/MMT composite films were obtained by casting the blend solution on glass substrates and drying in an oven at 70°C for 24h and then all the samples were dried for 8h at 70 °C under a vacuum. After being fully dried, the films were

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peeled off from those glass substrates, the thickness of the obtained films was in the range 0.05–0.1μm.

Sample Characterization

The melting and crystallization behavior of the PVA/MMT film samples were determined with a Netzsch DSC 200 (Germany) equipped with a cooling system in a nitrogen atmosphere. The instrument was calibrated for temperature and heat enthalpy with pure indium as the standard medium. About 2-5 *m*g of the sample was sealed in an aluminum pan, heated from room temperature to 230°C at a heating rate of 20 °C/min and held at that temperature for 5 min to eliminate the thermal history. The nonisothermal crystallization process was recorded at a cooling rate of 5°C/min, 10°C/min, 20°C/min and 40°C/min respectively from 230°C to 30°C. The endothermic and exothermic flows were recorded as a function of temperature. The pure PVA sample was treated by the same method for comparison.

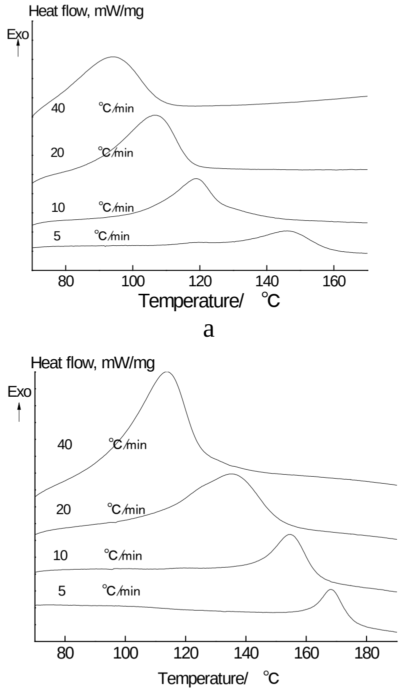
RESULTS AND DISCUSSION

DSC analysis is one of the most convenient and accurate techniques for determining the crystallinity of polymers[7-9]. Considering the crystalline essence of PVA, we can safely say that the change of crystallization and melting behaviors of PVA will take place due to the introduction of MMT and the alteration of the interface properties between them, which will affect the final properties of the composite. Owing to the melting point of MMT being much higher than 1400℃, whatever measurements were made by DSC show the properties of the PVA matrix only.

Figure 1 shows the DSC curves of the nonisothermal crystallization of pure PVA and the PVA/MMT composite at the cooling rates of °C/min, 10°C/min, 20°C/min and 40°C/min. The onset temperature (T_0) and the peak temperature (T_p) are listed in Table 1.

It can be seen that with the increase of the cooling rate, the crystallization peaks of the PVA and PVA/MMT composite shift from a high to a low temperature and the peak shapes become wide. This is mainly because the faster cooling rate can degrade the ordered arrangement of the molecular chain during the crystallization process, which makes nucleation lag behind and causes an initial crystallization delay. Finally, the crystallization peaks move from a high to a low temperature. Meanwhile, the faster cooling rate also leads to a worse mobility of the molecular chain. Then the imperfect crystals form, which results in a greater range of the crystallization temperature and wider crystallization peaks.

Compared with pure PVA, the crystallization temperature of the PVA/MMT composite is higher at any given cooling rate. This phenomenon can be explained by the heterogeneous nucleation effect of the MMT particles. As we know, the homogeneous nucleation of a material occurs spontaneously below the melting point and requires a long time. But the heterogeneous nuclei might be formed as soon as the material reaches its crystallization temperature. Therefore, the heterogeneous nucleation needs less time at the same cooling temperature.



a

b

Fig. 1. DSC thermograms of the nonisothermal crystallization for (a) pure PVA and (b) PVA/MMT composite at different cooling rates

To analyze the crystallization process even further, we have calculated the relative crystallinity $X_t$at any crystallization temperature (T) using the following equation:

$$X_t = \frac{\int_{T_0}^{T} (dH_c/dT)dT}{\int_{T_0}^{T_\infty} (dT_c/dT)dT} \quad (1)$$

where T_0 is the onset crystallization temperature, T_∞ is the temperature of crystallization termination and dH_c, the enthalpy of the crystallization released during an infinitesimal temperature change dT. In this case, the relationship between X_t and T can be obtained from the DSC data, corresponding to the crystallization peaks in Figure 1. Figure 2 shows the plots of the relative crystallinity versus the crystallization temperature for the PVA and PVA/MMT composite at different cooling rates.

It can be seen from Figure 2 that the crystallization processes of the PVA/MMT composite are over in a shorter time than for pure PVA. It has been known that the crystallization process of the polymer consists of the formation of nuclei and the growth of crystallites. Since MMT can work as crystallization nuclei and help the orderly distribution of PVA chains and crystal sheets, we can safely say that this effects both the formation of nuclei and the growth of crystallites.

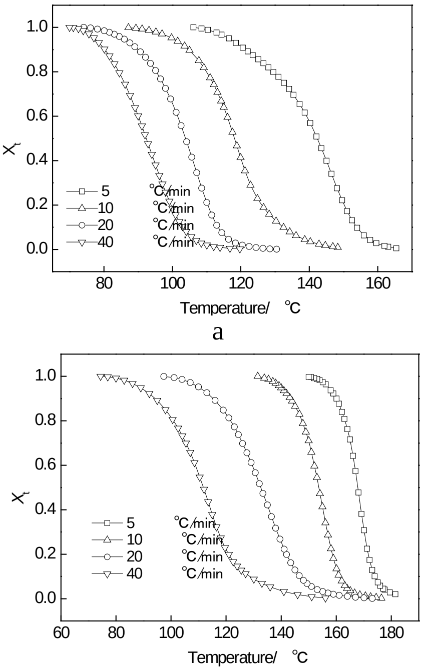


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Fig. 2. Plots of X_t versustemperature for crystallization of PVA (a)PVA/MMT(b)composite.

Many researchers use the method of DSC analysis to study the nonisothermal crystallization kinetics of polymers. They start from isothermal analysis and modify it, according to the characteristic of nonisothermal crystallization[10-11]. Every method has its application area and limitation. In this paper, we use the Jeziorny method[12] to analyze the nonisothermal crystallization kinetics of pure PVA and PVA/MMT composite.

The crystallization process can be expressed by the following Avrami equation:

$$1\text{-}X_t = \exp(-Z_t t^n) \qquad (2)$$

where $X_t$is the relative crystallinity at time t; n is the Avrami exponent related to the crystallization dimension, mechanism of nucleation and the form of crystal growth; and Z_t is the crystallization rate constant, which describes the nucleation and growth of the crystallites. The logarithmic analytic function of equation 2 is the following equation:

$$\ln[-\ln(1-X_t)] = \ln Z_t + n\ln t \qquad (3)$$

However, the Avrami equation indicates only the relationship of X_t and t, thus we have to convert the measurement temperature to time in accordance with the equation:

$$t = (T_0 - T)/\beta \qquad (4)$$

where t is the crystallization time; T_0 is the onset crystallization temperature; T is the crystallization temperature at time t and β is the cooling rate.

According to equation 4, the relationship between the relative crystallinity $X_t$and the crystallization time t can be obtained as shown in Figure 3.

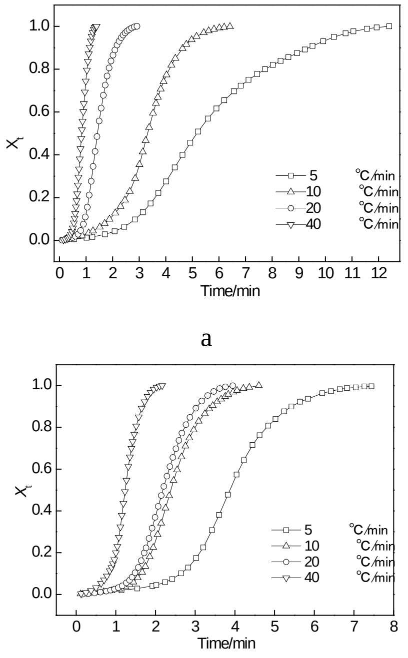

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Fig. 3. Plots of X_t versus time for the crystallization of PVA (a)PVA/MMT(b) composite.

The plots of ln[-ln(1-X_t)] versus ln$t$ for the pure PVA and PVA/MMT composite samples are shown in Figure 4. It is clearly seen from this figure that ln[-ln(1-X_t)] and ln$t$ show good linear relationships. The meaning is that the Jeziorny method can successfully describe the nonisothermal crystallization kinetics of the PVA and PVA/MMT composite under the given cooling rates.

The values of ln Z_t and n were obtained from the intercept and slope of these straight lines respectively in accordance with equation 3. Given the characteristics of the nonisothermal crystallization process, the Avrami equation is modified by the Jeziorny method and the constant logZ_t can be described as the following equation:

$$\log Z_c = \log Z_t/\beta \qquad (5)$$

where Z_c is the crystallization rate constant and β is the cooling rate. The calculated results are listed in Table 1.

$t_{1/2}$ is determined by the following equation:

$$t_{1/2} = (\ln 2/Z_t)^{1/n} \quad (6)$$

where the half time of crystallization ($t_{1/2}$) is the time required to reach 50% of the final crystallization. The values of $t_{1/2}$ are also listed in Table1.

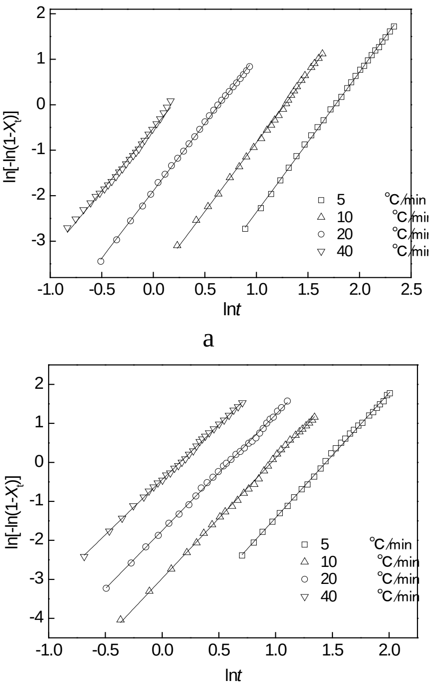

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Fig. 4. Plots of ln[–ln(1 – X_t)] versus ln*t* for crystallization of PVA (a) PVA/MMT(b)composite.

According to Table 2, T_0 and T_p of the PVA/MMT composite was higher than that of pure PVA, indicating that the addition of MMT can effectively increase the crystallization rate. With the increase in theβ values, T_0 and T_p shifted to a lower temperature region. The reason is that a high cooling rate can make the system become a part of a low temperature range fast and the low temperature can freeze the mobility of some segments, which leads to the growth of crystallization.

Obviously, the $t_{1/2}$ values of the PVA and PVA/MMT composite decreased with the increasing β values. Furthermore, the $t_{1/2}$ values of the PVA/MMT composite were smaller than those of pure PVA under the given cooling rates, it showed that MMT acted as an effective nucleating agent for the PVA and it can increase the crystallization rate of the PVA during the nonisothermal crystallization.

The Z_t andZ_c values of the PVA and PVA/MMT composite increased while *n* decreased with the increase in theβ values. Z_t, Z_c, *n* and ΔH_c of the PVA/MMT composite were higher than that of pure PVA under the given cooling rates, which indicates that the MMT can induce heterogeneous nucleation with a nonisothermal tridimensional growth of the spherulite.

CONCLUSIONS

The crystallization properties of pure PVA and PVA/MMT composite were studied by DSC analysis. The nonisothermal crystallization behavior of PVA/MMT composite was greatly affected by the loading of MMT. The PVA/MMT composite samples were found to have a shorter semicrystallization time $t_{1/2}$, a higher crystallization temperature T_0 and T_p, and crystallization enthalpy ΔH_c than that of pure PVA. The nonisothermal crystallization kinetics of pure PVA and PVA/MMT composite were analyzed by the Jeziorny method. The Avrami constants *n* and the crystallization rate constants Z_c were compared with the pure PVA. The results showed that the addition of MMT may significantly affect the nucleation and growth of PVA crystallization.

Table 1. Characteristic temperatures and kinetic parameters of nonisothermal crystallization for PVA and PVA/MMT.

	B (℃/min)	T_0 (℃/)	T_p (℃/)	Z_t	Z_c	n	$t_{1/2}$ (min)	ΔH_c (J/g)
PVA	5	168.12	146.01	0.004	0.336	3.08	4.67	-21.92
	10	148.33	118.91	0.021	0.680	3.03	3.33	-18.82
	20	132.47	106.53	0.151	0.910	2.96	2.19	-14.37
	40	125.84	94.55	0.593	0.987	2.74	1.24	-8.643
PVA/MMT	5	187.22	168.1	0.010	0.397	3.20	3.88	-25.39
	10	177.54	154.8	0.051	0.743	3.09	2.39	-24.62
	20	176.33	135.0	0.174	0.916	2.98	1.43	-19.95
	40	161.14	114	0.641	0.989	2.82	0.84	-16.37

REFERENCES

1. H.Q. Hong, H. He, Z.X. Jia, C. Ding, D.M.Jia, *J Appl Polym Sci*; **102**(4), 3889 (2006).
2. J. Li, C.X. Zhou, G. Wang, *Polym. Test.*, **22**(2), 217 (2003).
3. D.X. Li, D.M. Jia, P. Zhou, *J Appl Polym Sci.*, **93**(1), 420 (2004).
4. Y. Zhu, Z.C. Zhang, X.M.. Guan, *Journal of Thermoplastic Composite Materials*, **29**(5), 638 (2016).
5. W.B. Xu, G.D.Liang, H.B. Zhai, *Eur. Polym J.*, **39**(7), 1467 (2003).
6. H.Q. Hong, H. He, D.M. Jia, *Polym Polym Compos*, **16**(2), 131 (2008).
7. T.Z. Zhang, T. Li, N. Erik, *Polymer*, **50**(5), 1206 (2009).
8. P. Li; G.Yang, *Polymers for Advanced Technologies*, **27**(8), 1029 (2016).
9. G.S. Deshmukha; D.R. Peshwea; S.U. Pathaka; J.D. Ekheb, *Thermochimica Acta*, **606**, 66 (2015).
10. Q.X. Zhang, Z.H. Zhang, H.F. Zhang,Z.S. Mo, *J Polym Sci Polym Phys.*, **40**(16), 1784 (2002).
11. G. Xu; K. Min, *Polymer-Plastics Technology and Engineering*, **54**(4), 390 (2015).
12. A. Jeziorny, *Polymer*, **19**(10), 1142 (1978).

ИЗСЛЕДВАНЕ НА НЕИЗОТЕРМИЧНАТА КРИСТАЛИЗАЦИЯ НА КОМПОЗИТИ ОТ ПОЛИ-ВИНИЛОВ АЛКОХОЛ С МОНТМОРИЛОНИТ ЧРЕЗ ДИФЕРЕНЦИАЛНА СКАНИРАЩА КАЛОРИМЕТРИЯ (DSC)

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(Резюме)

Композитни филми от поли-винилов алкохол (PVA) с монтморилонит (MMT) са приготвени чрез леене от разтвор. Кристализацията в не-изотермични условия на PVA и на композитите PVA//MMTе изследвана чрез диференциална сканираща калориметрия (DSC). Установено е, че равномерно диспергираният MMT в матрицата има голямо влияние върху кристализацията на PVA. Приложен е Jeziorny-метода за анализа на DSC-данните. Резултатите показват, че, че този метод описав системата много добре. Сравнението показва, че композитът PVA//MMT има по-висока степен на кристалност спрямо PVA, по-кратко време на полу-кристализация $t_{1/2}$ и по-висока константа на кристализация Z_c. Може да се заключи, че MMT действа като ефективен acted заросиш-образуващ агент и има влияние върху растежа на кристалити при кристализацията с матрица от PVA.