



Simultaneous crystallization and decomposition of PVA/MMT composites during non-isothermal process



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ARTICLE INFO

Article history:

Received 13 May 2015

Received in revised form 10 August 2015

Accepted 8 September 2015

Available online 9 September 2015

Keywords:

Poly(vinyl alcohol)
Montmorillonite clay
Crystallization
Decomposition

ABSTRACT

Decomposition of poly(vinyl alcohol)/montmorillonite clay (PVA/MMT) composites during melting–crystallization was experimentally confirmed by morphology and molecular structure changes. In particular, FTIR spectra show the shift of O–H stretching band as well as enhanced intensities of C–O stretching and CH₂ rocking vibrational modes. Furthermore, Raman deconvolution indicates that C–H wagging, CH₂–CH wagging, CH–CO bending and CH₂ wagging modes in amorphous domains were all decreased greatly. Moreover, this decomposition leads to decreased melting enthalpy, melting point, crystallization enthalpy and crystallization temperature. Crystallization analysis shows that the MMT incorporated slows down the crystallization process in the PVA matrix regardless of the nucleation capability of MMT. Despite the severe decomposition, the crystallization kinetics still corroborated well with common classical models. As a result, molecular structure changes and crystallization retardation observed in this study clearly indicate the strong effects of the thermal degradation on the non-isothermal crystallization of PVA/MMT composites.

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1. Introduction

Polymer crystallization under different thermal conditions is of vital importance for the optimization of processing parameters in order to achieve certain specification in the finished polymer products [1]. In principle, the heat flow is produced over the course of the phase transition during crystallization, which can be monitored using differential scanning calorimetry (DSC) technique. Subsequently, the fundamental physical parameters that are of crucial importance for theoretical and applied research including crystallization rate [2], nucleation constant [3,4], equilibrium melting point [4–6], lateral and fold surface free energy [7], can be obtained using related physical modeling and mathematical processing approaches. In most productions, polymers are usually processed under dynamic, non-isothermal conditions such as extrusion. Therefore, insights into non-isothermal crystallization kinetics would lead to a deeper understanding to underpin further development of advanced composite materials based on polymer matrix.

In the past decades, there have been a number of reports studying the crystallization kinetics of poly(vinyl alcohol) (PVA) and PVA-based composites including partially hydrolyzed PVA [8], PVA/SiO₂ [9,10], PVA/carbon nanotubes [11,12], PVA/polyamide 6 blend [13], and PVA/attapulgitite [14]. While most reports focused on crystallization kinetics, only a few of them reported the possible degradation and its effects during the PVA crystallization [8,12,15,16]. Among them, Peppas and Hansen first reported that there was no evidence of degradation observed for PVA (99% hydrolysis) during an isothermal crystallization process [15]. Subsequently, a study claimed that an actual melting equilibrium was observed without any degradation of PVA using the high vacuum DSC method [16]. The report, however, led to a speculation on how one could achieve a high vacuum within the DSC cell [8]. In 2004, Probst et al. reported that there was degradation involved during the crystallization of PVA/carbon nanotubes based on the failed repeatability of crystallization exotherms at different cooling cycles [12]. Later on, Huang et al. found, based on their FTIR spectroscopic results, that there was no evidence of degradation observed for PVA (80% hydrolysis) during the DSC and suggested the necessity to carry out non-isothermal crystallization analysis [8]. Among a number of subsequent studies on the crystallization of PVA and PVA composites [15–18], experimental evidences showed that the non-isothermal crystallization of PVA–graphene composites is the

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combination of non-isothermal crystallization and non-isothermal degradation processes [17,18].

Layered montmorillonite (MMT) as a very widely distributed clay material is originated from the devitrification and chemical alteration of glassy volcanic ash or tuff [19]. It belongs to the group of expandable 2:1 layer silicate minerals and exhibits the composition $\text{Na}_x(\text{Al}_{2-x}\text{Mg}_x)(\text{OH})_2\text{Si}_4\text{O}_{10}$ (derived from $\text{Al}_2(\text{OH})_2\text{Si}_4\text{O}_{10}$) where the aluminum and magnesium ions occupy an octahedral sheet, between two tetrahedral silicate sheets [20,21]. Due to its non-toxicity, high strength, great abundance and low cost, MMT has been widely used for the fabrication of high performance polymer composites [22–25]. Yet, there was no investigation of the non-isothermal crystallization of PVA/MMT composites ever reported. In this study, the non-isothermal crystallization of PVA/MMT composites and its potential decomposition was systematically investigated for the first time using multiple-cycle DSC, FTIR and Raman techniques, to gain a better understanding into the crystallization mechanism of this particular composite material.

2. Experimental

2.1. Materials

PVA ($M_w \sim 145,000$ and 98–99% degree of hydrolysis) was purchased from Sigma–Aldrich (Sydney, Australia). Montmorillonite clay Cloisite® Na^+ (MMT) was provided by Southern Clay Products, Inc. (TX, USA). All other chemicals used in this study were of analytical grade.

2.2. Fabrication of PVA/MMT composites

Aqueous solutions of 5 wt.% PVA were prepared by dissolving PVA in deionised water for 3 h at 95 °C, which was then cast in a plastic Petri dish and dried in an oven at 40 °C for 3 days to obtain a homogenous reference film. For the fabrication of PVA/MMT composite films, 0.4% MMT was first dispersed in deionised water and stirred overnight to achieve a stable dispersion. This dispersion was then mixed with 5 wt.% PVA and stirred for 2 h to obtain a homogenous solution. The as-prepared mixed PVA–MMT solutions were finally cast in a plastic Petri dish and dried in an oven at 40 °C for 3 days to produce a homogenous film. The final content for MMT clay in the PVA matrix was kept approximately at 0.3% and 1.0%, which were referred as PM-0.3 and PM-1.0, respectively.

2.3. Non-isothermal melting–crystallization

The non-isothermal crystallization experiments were performed using a TA-DSC model Q200 instrument under nitrogen gas atmosphere. In practice, 7.0 ± 0.5 mg of polymer films (i.e. PVA, PM-0.3 and PM-1.0) were encapsulated in aluminum pans and sealed. All the samples were initially heated to a predetermined temperature at 245 °C and then kept isothermally for 5 min to remove any possible nucleation. After that, all the samples were cooled down at a cooling rate of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min, respectively, to determine the crystallization enthalpy of the polymers. Prior to the DSC test, all the polymer specimens were dried at 40 °C in an oven for 2 days.

To observe the weight loss during the melting–crystallization process, the above-mentioned non-isothermal crystallization experiments were repeated for 3 cycles using a TA-DSC model Q200 instrument under nitrogen gas atmosphere. In practice, 7.0 ± 0.5 mg of polymer films were encapsulated in aluminum pans and sealed. All the samples were initially heated to 245 °C at a heating rate of 15 °C/min and then kept isothermal for 5 min to remove any possible nucleation. After that, all the samples were cooled

down at a cooling rate of 20 °C/min. The weight loss percentage during the thermal treatment was defined as [18]:

$$W\% = \frac{(M_1 + M_2 - M_3)}{M_1} \times 100\% \quad (1)$$

where M_1 , M_2 and M_3 are the weight of the original polymer films, aluminum pans and the overall weight of the pan loaded with PVA or PVA/MMT composite film after the heat treatment, respectively. Since there are physically adsorbed water molecules in PVA macromolecules [26], the real weights of PVA or PVA/MMT composite films were corrected as:

$$M'_1 = M_1 \times \left(1 - \frac{\Delta H_{eva}}{2246.7}\right) \quad (2)$$

where M_1 is the real weight of polymer films, ΔH_{eva} ($\text{J}\cdot\text{g}^{-1}$) is the calculated evaporation entropy of the absorbed water in one gram PVA or PVA/MMT composite films (i.e. PVA, PM-0.3 and PM-1.0). Based on Eqs. (1) and (2), the weight loss percentage can be expressed as:

$$W\% = \frac{[M_1 \times (1 - (\Delta H_{eva}/2246.7)) + M_2 - M_3]}{M_1 \times (1 - (\Delta H_{eva}/2246.7))} \times 100\% \quad (3)$$

For each sample (i.e. PVA, PM-0.3 and PM-1.0), three specimens were tested and the average weight loss was used for the final analysis. All melting and crystallization entropies were integrated horizontally using TA Universal Analysis 2000 software.

2.4. Optical microscopy

Optical microscopic investigation of the PVA composites was carried out using a DP 70 Hi-Res Camera (Olympus, Japan). To investigate the morphological change during the non-isothermal crystallization process, some of the PVA composites were removed from the aluminum pans after the heating and cooling cycles previously performed in the DSC experiments. The results were compared to those of the original (untreated) samples.

2.5. Fourier transform infrared (FTIR) spectroscopy

FTIR experiments of the composite samples were performed on a Bruker Vertex 70 FTIR spectrometer (Bruker Optik GmbH, Ettlingen, Germany) equipped with a deuterated triglycine sulphate (DTGS) detector and a single-reflection diamond attenuated total reflection Fourier transform infrared (ATR-FTIR) sampling module (MIRacle™, Pike Technologies, Madison, WI). The spectra were acquired using 64 scans and 4-cm^{-1} resolution within a spectral range of $4000\text{--}600\text{ cm}^{-1}$. Spectral post-processing including baseline correction, normalization and deconvolution was performed using OPUS 7.0 software suite (Bruker Optik GmbH). All FTIR spectra presented in this work were baseline-corrected and subsequently vector-normalized prior to commencing spectral deconvolution.

2.6. Raman microspectroscopy

Raman measurements were conducted using a Renishaw InVia Raman Microspectrometer (Renishaw plc, Gloucestershire, UK), which was equipped with a 514-nm Ar^+ ion laser (Stellar-REN, Modu-Laser, LLC, Centerville, UT, USA), a 785-nm near infrared (NIR) laser (HPNIR, Renishaw plc, Gloucestershire, UK), and a thermo-electrical cooled CCD detector. The original laser power measured at the sample was reduced to 10–50% to prevent heating and photochemical damage to the samples. Acquisition parameters used for spectral data collection in most cases included 10 s exposure time and 4-cm^{-1} spectral resolution. Spectral post-processing consisting of baseline correction, smoothing, normalization and

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