Thermal stability, crystallization, structure and morphology of syndiotactic 1,2-polybutadiene/organoclay nanocomposite

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Received 1 September 2006; received in revised form 9 April 2007; accepted 23 April 2007
Available online 10 May 2007

Abstract

Syndiotactic 1,2-polybutadiene/organoclay nanocomposites were prepared and characterized by thermogravimetry analysis (TGA), X-ray diffraction (XRD), polarized optical microscopy (POM), and differential scanning calorimetry (DSC), respectively. The XRD shows that exfoliated nanocomposites are formed dominantly at lower clay concentrations (less than 2%), at higher clay contents intercalated nanocomposites dominate. At the same time, the XRD indicates that the crystal structures of sPB formed in the sPB/organoclay nanocomposites do not vary, only the relative intensity of the peaks corresponding to (010) and (200)/(110) crystal planes, respectively, varies. The DSC and POM indicate that organoclay layers can improve cooling crystallization temperature, crystallization rate and reducing the spherulite sizes of sPB. TGA shows that under argon flow the nanocomposites exhibit slight decrease of thermal stability, while under oxygen flow the resistance of oxidation and thermal stability of sPB/organoclay nanocomposites were significantly improved relative to pristine sPB. The primary and secondary crystallization for pristine sPB and sPB/organoclay (2%) nanocomposites were analyzed and compared based on different approaches. The nanocomposites exhibit smaller Avrami exponent and larger crystallization rate constant, with respect to pristine sPB. Primary crystallization under isothermal conditions displays both athermal nucleation and three-dimensional spherulite growth and under nonisothermal processes the mechanism of primary crystallization becomes very complex. Secondary crystallization shows a lower-dimensional crystal growth geometry for both isothermal and nonisothermal conditions. The activation energy of crystallization of sPB and sPB/organoclay nanocomposites under isothermal and nonisothermal conditions were also calculated based on different approaches.

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Keywords: Syndiotactic 1,2-polybutadiene; Crystallization; Clay; Differential scanning calorimetry; Polarized optical microscopy; Thermal stability

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1. Introduction

Syndiotactic 1,2-polybutadiene (sPB), first synthesized in 1955 by Natta and Corradini [1], is a thermoplastic elastomer of industry interest due to its adjustable properties from plastics to rubber. It has exhibited various practical applications, and can be used as films in packaging breathing items such as vegetables, fruits, crabs with puncture because of its higher carbon oxide gases and oxygen permeability and better resistance against wetting and slippage, rubber goods, molding applications such as molded bottles, adhesive, oil paint, photosensitive resin, plastics materials, tire treadings, tubes, hoses, and so on [2,3]. The various studies on sPB, thus, are useful from theoretical and industrial points of view. Recently, due to the discovery of new catalyst systems that can produce syndiotactic polymers with controllable constitution and configuration, many studies have been stimulated and some work on synthesis, thermal behavior, crystallization, structure and morphology of sPB have been published [4–8].

Nanocomposites consisting of polymer matrix and organoclay have gained great interest because of their unique mechanical, thermal, electrical and permeability properties compared to the pristine polymers [9,10]. Furthermore, the incorporation of nanoscale-layer clay into semi-crystalline polymers would dramatically influence the crystalline properties including crystallization kinetics, crystal structure and crystallinity. Nanoclay layer is an effective heterogeneous nucleating agent for decreasing the interfacial free-energy per unit area perpendicular to macromolecular chains, which enhances the nucleating speed and the crystallization, improves the cooling crystallization temperature, decreases the spherulite size; at the same time, a physical hindrance of nanoclay layers to the motion of polymer chains limits the crystallization of basal polymer, resulting in a decrease of crystallinity and degree of perfection of the crystal [10].

More often, isothermal crystallization is a common practice due to the convenience of theoretical treatment on the obtained data, however, isothermal crystallization are usually performed in a smaller temperature window. While, nonisothermal crystallization studies of polymers are more meaningful than isothermal crystallization study because it is similar to conventional industrial processing. There have several crystallization studies on pristine sPBs with different syndiotactic regularities [5–7], One of the authors have studied effects of atactic sPB on the crystallization of sPB [6], while pristine sPB has not been investigated in all respects of its crystallization behavior, for example, secondary crystallization. To the best of our knowledge, up to now, there are no studies of crystallization and thermal stability of sPB/organoclay nanocomposite.

In this study, we first prepared films of sPB and sPB/organoclay nanocomposites by in situ vacuum distillation of the solutions. And then, thermal stability, the clay dispersion states, isothermal and nonisothermal crystallization kinetics of pristine sPB and sPB/organoclay were investigated, respectively. The mechanisms of primary and secondary crystallization under isothermal and nonisothermal conditions were analyzed in terms of the parameters obtained. The thermogravimetry analysis (TGA), X-ray diffraction (XRD) and polarized optical microscopy (POM) were used to investigate thermal stability, crystalline structure and morphology of sPB and sPB/organoclay nanocomposites.

2. Experimental

2.1. Preparation of pristine sPB and sPB/organoclay samples

The synthesis and characterization of the sPB investigated have been described elsewhere [6].

The samples of syndiotactic 1,2-polybutadiene (sPB) were synthesized by using a new catalyst system, composed of iron(III) acetylacetonate (Fe(acac)$_3$), diethyl phosphite (DEP) and Al(i-Bu)$_3$. After the sPB was dissolved in trichlorobenzene (TCB), its molecular weight was determined by high-temperature gel permeation chromatography at 150 °C, to give a weight-average molecular weight ($M_w$) of $1.28 \times 10^6$ g mol$^{-1}$ and $M_w/M_n$ of 2.42.

The organoclay in this work was cloisite 20A (Southern Clay Product Inc). It was a montmorillonite organically modified with dimethyl dehydrogenated tallow quaternary ammonium in order to increase the gallery spacing of the original Na$^+$–montmorillonite. The Cation exchange capacity (CEC) of the clay was 95 mequiv/100 g. For the preparation of sPB/organoclay nanocomposite, we used a technique different from conventional solution casting and melt mixing techniques. The sPB samples were first weighted to prepare toluene solutions of 10% sPB weight concentration, after the sPB samples were dissolved in toluene at 100 °C.
(a temperature near the boiling point of toluene), organoclays with different weight ratios were added to the solutions; a magnetic stirrer was then put into the solution to let organoclay mechanically blended for 24 h at 100 °C with nitrogen purge protection, followed by vacuum distillation of the solutions for another 12 h without moving the magnetic stirrer. As a matter of fact, due to high volatility of toluene under the conditions of vacuum distillation at 100 °C, toluene in the solutions was taken away in a few minutes. The obtained sample films were then subjected to pressing under pressure of 15 MPa at 210 °C between polytetrafluoroethylene films and were naturally cooled down to room temperature. The sheets were then used for XRD and POM measurements.

2.2. Thermogravimetry analysis

A Perkin–Elmer (PE) Pyris 1 TGA was used to investigate the thermal stability of the films of sPB and sPB/organoclay nanocomposites. The samples with weight 3.0 ± 0.3 mg were heated at 20 °C/min from 100 °C to 700 °C under air purge and argon purge, respectively. The data analysis was performed with the provided software of this computer. For confirmation, repeated experiments were performed, good repetitions were observed.

2.3. DSC measurements

A Perkin–Elmer (PE) diamond DSC calibrated with indium and zinc standards was used to monitor the crystallization and melting behaviors of the sPB and sPB/organoclay. All operations were performed under nitrogen purge. Sample weight for each experiment is 4.0 ± 0.3 mg.

(I), the sample films obtained from the solutions by vacuum distillation were subjected to two scanning circles: first the samples was heated at 20 °C/min from 50 °C to 200 °C (first heating), kept at 200 °C for 3 min, cooled at 20 °C/min from 200 °C to 50 °C (first cooling), stayed at 50 °C for 3 min, heated at 20 °C/min from 50 °C to 200 °C (second heating), kept at 200 °C for 3 min, and then cooled at 20 °C/min from 200 °C to 50 °C (second cooling).

(II), for studying the isothermal crystallization of sPB and sPB/organoclay, the following procedures are followed: first the samples were heated to 200 °C, kept at 200 °C for 3 min to eliminate the thermal history of this sample, then cooled at 100 °C/min to the preset temperature to let sample crystallize, the heat flow was recorded with crystallization time.

(III) The experiments of nonisothermal crystallization of sPB/organoclay (2%) were performed as follows: first the samples was heated at 100 °C/min from 50 °C to 200 °C, kept at 200 °C for 3 min to eliminate the thermal history of this samples, followed by cooling at different rates – 5 °C/min, 7.5 °C/min, 10 °C/min, 15 °C/min, 20 °C/min to 50 °C.

The melting peak temperature and the heat of fusion were calculated by the supplied software of the DSC instrument.

2.4. POM measurements

The morphology of various thin film samples of sPB and sPB/organoclay (2%) was observed and compared by using a polarized optical microscope (Leika) equipped with a Leika automatic thermal control hot-stage (with the controlling temperature precision of ±0.1 °C), a JVC model digital-color-video camera, a liquid-nitrogen cold-trap, and a computer. The sPB and sPB/organoclay sheets with thickness of 30 μm were sandwiched between microscope cover glass and heated to 200 °C, then rapidly cooled at 80 °C/min to the designated temperature (as an example, 148 °C was selected for morphology comparison of pristine sPB and sPB/organoclay (2%), for other temperatures the difference of pristines sPB and sPB/organoclay (2%) were similar), and held there for observing morphology development of isothermal crystallization. The JVC model digital-color-video camera on the Leika POM instrument and an installed software in the computer were used to in situ record and save the spherulitic morphology at due interval time in the computer.

2.5. X-ray measurements

X-ray diffraction experiments were performed by using a Rigaku D/max 3C diffractometer with curved graphite crystal-filtered CuKα1 radiation (λ = 0.15406 nm). The sheet specimens were fixed on the rotating sample stage of the goniometer in order to eliminate any anisotropic effects, and so that suitable averages of the diffracted intensities in reciprocal space could be obtained. Data were collected over the range 2θ = 1–40° in the fixed time mode with a step interval of 0.02°. For better obtaining information of data in the wide angle
range of 1–40°, the data of 1–10° and 10–40° were collected, respectively. The X-ray diffraction experiments were performed under ambient conditions on the organoclay and the sheets of sPB/organoclay with different ratios subjected to melt-pressing at 200 °C to evaluate the dispersion states of clay sheets and the structure of sPB in sPB/organoclay nanocomposites.

3. Results and discussion

3.1. X-ray diffraction (XRD)

For investigating dispersion states of organoclay nano-sheets in sPB matrix, the XRD experiments of sPB/organoclay nanocomposites with different organoclay concentrations range from 0.5% to 8% were performed and shown in Fig. 1a. For comparison, the XRD data of Cloisite 20A organoclay were also drawn in Fig. 1a. The 2θ angle range is 1–10° in Fig. 1a. For Cloisite 20A organoclay, two peaks located at 3.7° and 7.3°, respectively, are found. The relative weaker peak at 7.3° possibly corresponds to the basal spacing of the clay aggregates, ca. 1.2 nm and the peak located at 3.7° corresponds to the gallery spacing of organoclay with 2.4 nm. As weight percent of the organoclay are 0.5% and 1%, no distinct X-ray diffraction peak was observed (Fig. 1a), indicating the delamination and dispersion of clay nanoclay into sPB matrix. As the concentration of organoclay was increased to 2%, the peak at 7.3° for original organoclay also disappears and the peak at 3.7° shifts to lower angle, splitting into two peaks, which are located at 2.5° and 3.1°, respectively. The two peaks correspond to spacing of 3.5 nm and 2.8 nm, which indicates the existence of intercalated clay due to the entrance of sPB chains into the gallery of organoclay. As the organoclay content was increased to 4%, a wide peak located at 2.6°, corresponding to 3.4 nm, exists. As the content of organoclay was 8%, it can be observed that one strong peak at 2.8° with a shoulder peak at 3.9° exists. Fig. 1a also indicates that the positions for peaks at lower angles increase with increasing the content of sPB samples, indicating the increment of the gallery spacing of organoclay with increasing sPB concentration. It is noteworthy that for concentrations of organoclay with 0.5% and 1%, although no distinct diffraction peak was observed, there exists a wide shoulder peak in the small-angle region, which could not exclude the existence of intercalated structures, therefore, possibly indicating the existence of partially exfoliated/partially intercalated nanostructures in these sPB/organoclay nanocomposites. It seems reasonable that Kojima et al. [11] characterized the relative proportion of exfoliated and intercalated species with the content of nanoclay using the peak intensity together with the interlayer spacing (i.e., the peak position). Here from the XRD patterns of sPB/organoclay, it is possible that the exfoliated structure is the dominant population as the content of organoclay is below 2%, and above it, the intercalated hybrids gradually dominate.
And between the two extremes, exfoliated structure with partially structure order is likely formed [12].

Fig. 1b indicates the XRD patterns for sPB/organoclay with different content of organoclay in the 2θ angle range of 10–40°. For comparison purpose, the XRD data of the organoclay and pristine sPB sample were added into Fig. 1b to observe the possible variation. For pristine sPB sample, there existed five distinct diffraction peaks, the peak intensity decreases with increment of peak position. The diffraction angles at the maximum intensities correspond to interplanar distances of 0.655, 0.549, 0.420, 0.380, 0.318 nm according to the sequence from low to high angles. The values are close to those reported by Natta and Corradini [1]. According to the orthorhombic cell unit packing of the sPB sample proposed by these authors, the indices for the peaks from low to high angles correspond to (010), (200)/(110), (210), (111)/(201), and (120). Interestingly, as organoclay contents are 0.5% and 1%, the peak of (111)/(201) crystal plane is very weak, with the other four peaks being clearly observed. While as organoclay content is increased to 2%, the (111)/(201) peak again appears, above 2%, the peak intensity gradually increases. In addition, with increasing the concentration of organoclay, the relative intensity of peaks corresponding to (010) and (200)/(110) crystal planes varies, as the content of organoclay is below 2%, the intensity of (010) peak is stronger than that of (200)/(110) peak. While as the content of organoclay reaches 4%, the relative intensity of the two peaks reverses, the intensity of (010) peak is weaker than that of (200)/(110) peak. In our previous work [6], it was found that atactic 1,2-polymer chains could affect the relative intensity change of XRD peaks of syndiotactic 1,2-polybutadiene. Initiated by our experimental work [6], Napolitano et al. [8] have contributed the intensity change of peaks to the presence of configurational defects in the crystal phase by comparing the experimental and simulated XRD profiles obtained by using program Cerius² software. While that the intensity of (111)/(201) peak for sPB/organoclay nanocomposites with 0.5% and 1% organoclay becomes so weak is still kept inexplicit, the mechanism study of peak intensity change is in progress. Although the peak intensity change with organoclay content was observed, but the peak positions were kept almost unchangeable, this is to say, the crystal structure of sPB sample does not change due to the addition of organoclay, only affecting the crystal perfection formed.

4. Thermogravimetry analysis (TGA)

The thermal stabilities of pristine sPB and nanocomposites have been investigated by TGA under Argon and air flows, respectively. Since the practical application is under air atmosphere, here, we only show the traces under air purge (Fig. 2). The decomposition temperatures for weight loss of 10% in both argon ($T_{0.1-\text{Argon}}$) and air ($T_{0.1-\text{air}}$) are collected and listed in Table 1. Table 1 indicates that under argon flow the decomposition temperature indicates a little decrease, especially for 8% organoclay content, the $T_{0.1-\text{Argon}}$ decreases from 441.4 °C to 424.7 °C. While under air flow the nanocomposites indicate improved thermal stability. $T_{0.1-\text{air}}$ distinctly increases from 336.5 °C for pristine sPB to the range between 430.3 °C and 444.9 °C, depending on the content of organoclay for nanocomposites. For confirmation, the data of these samples were performed again, good repetitions were observed. Since practical processing is under air atmosphere, organoclay is a possible candidate to improve the thermal stability of sPB materials.

At the same time, it can be observed from Fig. 2 that the TGA curve for pristine sPB is a little different from those of nanocomposites under air purge. At 183.6 °C, the weight percent of pristine sPB sam-

![Fig. 2. Thermogravimetric curves of sPB/organoclay with different contents as indicated under air purge at a heating rate of 20 K/min.](image-url)
ple quickly increases from 100% to 109.8%, this is possibly due to the occurrence of oxidation reaction of the vinyl group in air atmosphere (The conclusion was drawn from the following facts: one is that, under nitrogen flow, we could not observe the phenomena of weight addition with increasing temperature, the other is that under air atmosphere the weight-adding phenomena could be observed, indicating that oxidation reaction occurs on the sPB chains under air atmosphere at higher temperature. In addition, thermogravimetry data of low density polyethylene (LDPE) under air atmosphere (the graph is not shown here) indicate that there is no weight change before 261 °C (\textasciitilde 183.6 °C – the onset of weight addition of sPB), indicating that the methylene, methine on the sPB chain does not contribute to the oxidation reactions of sPB samples. And, furthermore, a FTIR experiment (not shown as well) was designed to indicate that after the sPB sample was heated at 20 °C/min under air atmosphere to 220 °C, stay at the temperature for 12 s, and then cooled to room temperature at 10 °C/min, at 1721 cm$^{-1}$, an additional peak attributed to oxidation reactions of vinyl groups appears in the FTIR spectroscopy relative to FTIR data of the sPB sample without subjecting to heating at high temperature. These facts indicate that the weight-increasing is due to oxidation of vinyl groups of sPB chains. But further details need more experimental supports, the related works are in progress). And then at 264.7 °C the weight of the pristine sPB begins to decrease, until 535 °C is reached, at which the sample is decomposed completely. For nanocomposites, the onset temperature of the weight increase due to oxidation was greatly delayed, furthermore, the increase amplitude in weight decreases greatly from 109.8% for pristine sPB to the range between 100.4% and 102.4% depending on the content of organoclay. This means that during heating the chance of vinyl groups along the sPB chain being oxidized was greatly reduced due to the existence of nanoclays. The data of the onset oxidation temperature ($T_{\text{onset oxidation}}$) and the maximum weight increase ($T_{\text{end oxidation}}$) due to oxidation were also listed in Table 1, together with $T_{0.1}$-argon and $T_{0.1}$-air.

5. Differential scanning calorimetry

5.1. Effects of organoclay content on crystallization and melting

The films obtained by vacuum distillation at 100 °C were subjected to 2 heating/cooling DSC circles, good repeated curves for first and second cooling scans were observed, indicating that staying at 200 °C for 3 min could eliminate the previous thermal history of pristine sPB and sPB/organoclay nanocomposites. The first heating curves for sPB blended with different content organoclays (0.5%, 1%, 2%, 4%, 8%) were indicated in Fig. 3a. For comparison, the heating curves for pristine sPB films obtained by vacuum distillation at 100 °C (indicated as number ‘1’) and melt crystallized at 100 °C for 2 h (indicated as number ‘0’), respectively, were added into Fig. 3a as well. It indicates that melting temperatures of the samples obtained from the solutions by vacuum distillation at 100 °C are far higher than that obtained from melt-crystallization at 100 °C, indicating more perfect crystals formed from toluene solutions at 100 °C than those obtained from the melt-crystallization at the same temperature, the conclusion can also be supported by the second heating curves, which indicate apparent decrease of melting peak temperature relative to the first heating curves (Fig. 3a and b). The melting temperature parameters for the first and second heating curves are collected and summarized in Table 2. Except the difference of crystal perfections between solution- and melt-crystallization, it was surprising to find that the melting enthalpies obtained from toluene solutions are far higher (55.4 ± 3.5 J/g) than those obtained from melt-crystallization (36.8 ± 2.4 J/g), increasing by ca. 50%. The melting

<table>
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<tr>
<th>Content of clay (%)</th>
<th>$T_{0.1}$-Argon (°C)</th>
<th>$T_{0.1}$-Oxygen (°C)</th>
<th>$T_{\text{Onset oxidation}}$ (°C)</th>
<th>$W_{\text{End oxidation}}$ (%)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>441.4</td>
<td>336.5</td>
<td>183.6</td>
<td>109.8</td>
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<tr>
<td>0.5</td>
<td>436.1</td>
<td>442.6</td>
<td>210.1</td>
<td>100.6</td>
</tr>
<tr>
<td>1</td>
<td>441.6</td>
<td>444.9</td>
<td>216.3</td>
<td>100.4</td>
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<td>442.7</td>
<td>207.6</td>
<td>101.9</td>
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<td>8</td>
<td>424.7</td>
<td>430.3</td>
<td>202.2</td>
<td>102.4</td>
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</table>

Table 1
Thermogravimetry analysis parameters of sPB/organoclay with different contents
enthalpies were also listed in Table 2. The melting enthalpy for pristine sPB melt crystallized at 100 \(^\circ\)C for 2 h was calculated from the higher melting peak without considering the contribution of the lower temperature melting peak, which is due to the formation of thinner and less perfect crystals [13]. In addition, for the second heating curve of sPB with 1% organoclay, a shoulder peak, as shown with an arrow, appears; Table 2 also indicates that for both the first and second heating curves, below 1% organoclay, melting peak temperature (\(T_{\text{mp}}\)) increases with content of organoclay, above 1%, \(T_{\text{mp}}\) decreases by 1–2 \(^\circ\)C with increasing concentration of organoclay.

Fig. 4 compares heat flow development during cooling at 20 \(^\circ\)C/min for sPB/organoclay nanocomposites. The corresponding crystallization parameters extracted and listed in Table 3 are the onset crystallization temperature (\(T_{\text{onset}}\)), end crystallization temperature (\(T_{\text{end}}\)), peak temperature (\(T_{\text{mp}}\)), the full width at half height of the exothermic peak (\(T_{\text{WHH}}\)), and crystallization exothermic enthalpy (\(\Delta H\)). Table 3 indicates that as 0.5% organoclay

<table>
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<tr>
<th>Content of clay (%)</th>
<th>(T_{\text{peak}}^a) ((^\circ)C)</th>
<th>(\Delta H^a) (J/g)</th>
<th>(T_{\text{peak}}^b) ((^\circ)C)</th>
<th>(\Delta H^b) (J/g)</th>
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<td>169.93</td>
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</table>

\(a\) First heating.
\(b\) Second heating.
\(c\) Pure sPB melt crystallized at 100 \(^\circ\)C for 2 h.
was added into sPB matrix, \( T_{\text{onset}}, T_{\text{end}}, T_p \) distinctly improved, \( T_{\text{WHH}} \) decreases from 9°C to 7.5°C, and \( \Delta H \) decreases slightly; increasing the content of organoclay in the sPB matrix, \( T_{\text{onset}}, T_p \) increase slightly, \( T_{\text{end}} \) and \( \Delta H \) vary little, and \( T_{\text{WHH}} \) decreases until the content of organoclay reaches 4% and becomes level off above 4%. These data indicates that the organoclay affects greatly the crystallization of sPB during cooling from the melt.

5.2. Isothermal crystallization

For further studying effects of organoclay on crystallization of sPB, the nanocomposites of sPB/organoclay (2%) were selected for comparison with pristine sPB. Five crystallization temperatures (146°C, 148°C, 150°C, 152°C, 154°C) were chosen. Fig. 5 gives the dependence of relative crystallinity \( X(t) \) for sPB/organoclay (2%) on crystallization time at five different temperatures. About 60 data points for each crystallization temperature are shown as geometrical points. It is clear that the time to reach the ultimate degree of crystallinity increases with increasing crystallization temperature, \( T_c \). The crystallization-half time, \( t_{1/2} \), the important crystallization parameter, is defined as the elapsed time from the onset of crystallization until the crystallization reaches half of the whole crystallization contribution, it can be obtained directly from Fig. 5. Table 4 listed the \( t_{1/2} \) data from Fig. 5. At the same time, the isothermal crystallization-half time, \( t_{1/2} \), for pristine sPB at the five temperatures are summarized in Table 4. It can be observed that \( t_{1/2} \) values for both pristine sPB and sPB/organoclay (2%) increase with increasing \( T_c \) at the studied temperature range; furthermore, the \( t_{1/2} \) for pristine sPB is larger than that for sPB/organoclay (2%) at the same crystallization temperature. Generally, the rate of crystallization can be described as the reciprocal of \( t_{1/2} \). Thus, this indicates that the crystallization rate of sPB/organoclay (2%) is faster than that of pristine sPB at the same crystallization temperature, and the crystallization rate for both pristine sPB and sPB/organoclay (2%) decreases with increasing crystallization temperature, characteristic of nucleation-controlled process.

The whole crystallization process of a semi-crystalline polymer is generally separated into two main stages: primary crystallization and secondary crystallization. And primary crystallization is the macroscopic development of crystallinity degree due to two consecutive microscopic mechanisms, i.e., primary nucleation and subsequent crystal growth. The primary process of isothermal crystallization of a polymer can be described by the well-known Avrami equation [14,15]:

\[
X_t = 1 - \exp(-kt^n)
\]  

where \( X_t \) is the relative crystallinity at time \( t \), \( k \) is crystallization rate constant, and \( n \) is the Avrami exponent which indicates the nucleation mechanism and growth dimensions. Depending on the mechanism of nucleation and type of crystal growth, different integer values of \( n \) can be obtained.

As the Avrami equation only hold well in the early stages of isothermal crystallization, the data analysis based on the Avrami model was performed by directly fitting the early \( X_t \) for each crystallization temperature to Eq. (1). The kinetic parameters of pristine sPB and sPB/organoclay (2%) could be obtained by using the non-linear regression method. The standard deviation (SD) is defined as [16]:

![Fig. 5. The relative crystallinity development with crystallization time for sPB/clay (2%) at different temperatures. The dotted and solid lines are the calculated ones from the standard and series-parallel Avrami models, respectively.](image-url)
The fractional value of $n$ obtained from experimental data is due to the various simplifications assumed in the original derivation of Avrami equation which do not necessarily apply to all polymer systems under all crystallization conditions [13]. In this study for pristine sPB and sPB/organoclay (2%), the $n$ values for sPB range from 2.21 to 2.92 and those for sPB/organoclay (2%) from 2.07 to 2.33, indicating three-dimensional growth by athermal nucleation mechanism during primary crystallization. For the same crystallization temperature, sPB/organoclay (2%) characterizes smaller $n$ value, indicating that the organoclay acted as nucleation agents during primary crystallization process.

The values of the crystallization rate constant $k$ for both pristine sPB and sPB/organoclay (2%) decrease with increasing $T_c$, and $k$ for pristine sPB is smaller than that for sPB/organoclay (2%) at the same temperature. From Arami exponent $n$ and crystallization rate constant $k$, the crystallization time $t_{1/2}$ can be calculated using the following formula:

$$t_{1/2} = \left( \frac{\ln 2}{k} \right)^{1/n}$$  

(3)

The obtained kinetic parameters ($n$ and $k$), along with the corresponding SD values for pristine sPB and sPB/organoclay (2%), are summarized in Table 4. The fractional value of $n$ obtained from experimental data is due to the various simplifications assumed in the original derivation of Avrami equation which do not necessarily apply to all polymer systems under all crystallization conditions [13]. In this study for pristine sPB and sPB/organoclay (2%), the $n$ values for sPB range from 2.21 to 2.92 and those for sPB/organoclay (2%) from 2.07 to 2.33, indicating three-dimensional growth by athermal nucleation mechanism during primary crystallization. For the same crystallization temperature, sPB/organoclay (2%) characterizes smaller $n$ value, indicating that the organoclay acted as nucleation agents during primary crystallization process.

Secondary crystallization is mainly concerned with the crystallization of interfibrillar, crystallizable melt, which has been rejected and trapped between the fibrillar structures. The model of the secondary crystallization occurring with spherulites was first suggested by Hiller [17] and Price [18] to analyze the isothermal crystallization data of high performance polymers such as poly(ether ether ketone) (PEEK), poly(ether ketone ketone) (PEKK) and poly(phenylene sulfide) (PPS). Velisaris and Seferis [19] proposed a parallel Avrami model to consider secondary crystallization. By considering inter- and intra-spherulite in the secondary process, a ‘series–parallel’ Avrami model was recently proposed by Woo and Yau [20]. The primary crystallization is assumed to hold the following relationship:

$$X_t = \omega_p [1 - \exp(-k_p t^n)]$$  

(4)

The secondary crystallization which occurs at $t > t_d$ is assumed to hold the following relationship:

$$X_t = \omega_p [1 - \exp(-k_p t^n)] + \omega_s [1 - \exp(-k_s (t - t_d)^{n_s})]$$  

(5)

where the subscript ‘p’ indicates the primary crystallization starting at $t = 0$ and the subscript ‘s’ indicates the secondary crystallization starting at $t = t_d$ (the latter being the onset time of secondary crystallization); $n_p$, $n_s$ are the Avrami exponents, $k_p$ and $k_s$ are the rate constants, and $\omega_p$, $\omega_s$ are the mass fractions, in all cases for the primary and secondary crystallization, respectively. Apparently, $\omega_s = 1 - \omega_p$.

For obtaining the kinetic parameters in Eq. (5), $t_d$, the onset time of secondary crystallization, should be first obtained. Lu and Hay [21] obtained $t_d$ by adjusting the relative crystallinity at the end of the primary process until the Avrami exponent remained essentially constant. Rybniker [22] proposed that $t_d$ was in agreement with the value of the two half-times of primary crystallization, i.e., the end of primary crystallization. Woo and Chen
suggested that \( t_d \) was defined as the time at which the discontinuity in the Avrami plot was located. In this study, we have adopted the latter method to extract the \( t_d \) of sPB and sPB/organoclay (2%) at different crystallization temperatures. As shown in Fig. 6, the primary and secondary crystallization processes occurred consecutively and were separated at the critical time of \( t_d \), when a sudden change of the slope, i.e., the Avrami exponent, from ca. 2.1 to 1.3 occurred.

Data analysis based on the ‘series–parallel’ Avrami model was carried out by fitting the experimental \( X_t \) data obtained for each temperature to Eqs. (4) and (5). The kinetic parameters, along with the SD values calculated for \( X_t \) ranging from 0.01 to 0.99 are listed in Table 5. The values of \( n_p \) vary from ca. 2.1 to 2.5 for sPB/organoclay (2%) and from 2.3 to 2.7 for pristine sPB. and the values of \( n_s \) range from ca. 1.1 to 1.5 for sPB/organoclay (2%) and from 1.3 to 1.6 for pristine sPB. Comparing the values of \( n_p \) and \( n_s \) between pristine sPB and sPB/organoclay (2%), pristine sPB has larger values. For both sPB and sPB/organoclay (2%), \( n_s \) is always smaller than the \( n_p \) at the same temperature, this is due to the fact that the growth geometry of crystal is restricted because of impingement and confinement of crystals formed during primary crystallization process. Thus the crystals grow in lower dimension between the fibrillar structures during the later stage.

The values of \( k_s \) for both pristine sPB and sPB/organoclay (2%) depend on the \( T_c \) and change in same trend as the values of \( k_p \) for the primary crystallization. Whether \( k_p \) or \( k_s \), the smaller values of \( k_p \) and \( k_s \) for pristine sPB are characterized relative to those for sPB/organoclay (2%). The \( \alpha_p \) decreases with the increasing \( T_c \) for both pristine sPB and sPB/organoclay (2%), this indicates that a faster primary crystallization process was accompanied by a decrease in the mass fraction for secondary crystallization. It is noteworthy that the time for the onset of secondary crystallization \( t_d \) increases with \( T_c \), except for 148°C and 150°C of sPB/organoclay (2%), as shown in Table 5. Comparing the \( t_d \) and the \( t_{peak} \)(the time at which the maximum crystallization rate is reached), \( t_d \) is larger than \( t_{peak} \). This is in good agreement with the assumption of Karmal and Chu [24] that secondary crystallization starts after \( t_{peak} \) for polyethylene samples.

The calculated curves using the ‘conventional’ Avrami model and the ‘series–parallel’ Avrami model were drawn, as sPB/organoclay (2%) samples were selected as an example, the calculated curves and experimental data were compared (as shown in Fig. 5). It indicates that the ‘series–parallel’

![Fig. 6. A typical representation of the onset time of secondary crystallization \( t_d \) during isothermal crystallization process of sPB/ clay (2%) at 146°C.](image)
Avrami model fits better with the experimental data than the ‘conventional’ Avrami model does.

As the crystallization process is assumed to be thermally activated, the crystallization rate constant \( k \) can be approximately described in the Arrehenius form, as follows [25]:

\[
k^{1/n} = k_0 \exp(-\Delta E/RT_c)
\]

or

\[
\frac{1}{n} \ln k = \ln k_0 - \Delta E/RT_c
\]

where \( k_0 \) is the temperature-dependent pre-exponential factor, \( \Delta E \) is the total activation energy which includes the transport activation energy and nucleation activation energy at the crystallization temperature \( T_c \). \( R \) is the universal gas constant. The activation energy \( \Delta E \) can be determined by multiplying \(-R\) of slope obtained by fitting linear the plot of \( 1/n \ln k \) versus \( 1/T_c \). With this technique, the kinetic parameters for primary and secondary crystallization process are analyzed and listed in Table 5 (Fig. 7). The values of the activation energy for primary and secondary crystallization of pristine sPB and sPB/organoclay (2%) were determined to be \(-440 (\pm 665) \text{ kJ/mol}, -275.9 (\pm 479) \text{ kJ/mol}\), respectively. The values in the bracket designate those of the secondary crystallization. It is clear that whether pristine sPB or sPB/organoclay (2%), the \( \Delta E \) for the secondary crystallization is larger than that for the primary crystallization process, so indicating that secondary crystallization from the crystallizable melt in the interfibrilles is more difficult than primary crystallization from the melt. This observation was interpreted as follows. With the crystallization process proceeding, rejection of the non-crystallizable material is also concentrated between the interfibrilles, which impeded diffusion of the crystallizable material Thus, the secondary crystallization became difficult due to the impeded diffusion of the crystallizable species and by a hindering mechanism between interfibrilles. Bertini et al. [5] have reported the value of activation energy \(-509 \text{ kJ/mol}\) for primary crystallization process of a sPB with higher syndio-regularity, based on Arrhenius analysis.

In the case of isothermal crystallization, the true link of the obtained Avrami exponent from DSC measurement and crystallization mechanism can be further examined by morphological observations, for example, by polarized optical microscopy. So in this study, we investigated the morphology of sPB and sPB/organoclay (2%) using polarized optical microscopy (POM). The representative end morphologies of sPB and sPB/organoclay (2%) crystallized at 148 °C for 30 min were shown in Fig. 8. For sPB, the diameters of the spherulites range from 40 to 80 \( \mu \text{m} \), while, for sPB/organoclay (2%) the diameters of the spherulites become more uniform and smaller, as expected. Comparing the linear growth rate of the spherulites of sPB and sPB/organoclay (2%) at the same crystallization temperature, the growth rate of sPB/organoclay (2%) was greatly enhanced. For other crystallization temperatures, the same difference between sPB and sPB/organoclay (2%) was observed. In this study, because the thickness of DSC films is approximately 300 \( \mu \text{m} \), far larger than the final spherulite diameter. Therefore, it is confirmed that the isothermal crystallization processes of sPB and sPB/organoclay (2%) investigated by DSC measurement exhibit three-dimensional spherulite growth rather than two-dimensional spherulite growth.

### 5.3. Nonisothermal crystallization

Several nonisothermal studies of sPB with different syndio-regularity have been reported [5–7]. In this section, we will investigate nonisothermal crystallization process of sPB/organoclay (2%) to investigate effects of added organoclay on crystallization of sPB. Fig. 9 presents the nonisothermal DSC curves of sPB/organoclay (2%). The corresponding parameters obtained from these curves are summarized in Table 6. \( T_o \) and \( T_e \) represent the onset temperature of crystallization and the end temperature of crystallization, respectively. \( T_p \) is the peak temperature.

![Fig. 7. Arrhenius plots for sPB/clay (2%) and pure sPB. ■, primary crystallization; ●, secondary crystallization.](image-url)
temperature at which the crystallization rate was at the maximum. The time $t_{\text{max}}$ corresponds to $T_p$, and $\Delta H_c$ is the crystallization enthalpy. It can be seen that the $T_0$, $T_e$, $T_p$ shift to a lower temperature region. This indicates that the mechanism of crystallization of sPB/organoclay (2%) is dependent on the cooling rate: at higher cooling rates, the activation of nuclei occurs at lower temperatures, whereas when the samples are cooled at lower cooling rates, crystallization occurs at higher temperatures.

Fig. 10 indicates the temperature-dependence of relative crystallinity function $X_t$ at different cooling rates. The relationship between the temperature $T$ and time $t$ can be established by:

$$t = \frac{T_0 - T}{\phi}$$

where $T$ is the temperature at time $t$, $T_0$ is the onset crystallization temperature (the temperature at which heat flow change of DSC exothermic curve can be detected, $t = 0$). The temperature abscissa axis shown in Fig. 10 can be transferred into a time scale (Fig. 11). It shows that increasing cooling rate results in shorter time for crystallization to be completed.

Nonisothermal crystallization theory and methods can have practical significance both in the simulation of technological processes and in the determination of parameters of the crystallization kinetics of polymers. For obtaining the kinetic parameters of crystallization kinetics of polymers, several formulæ have been suggested [26–29], most based on the ‘conventional’ Avrami model. Although the Avrami equation is often used to study the isothermal crystallization behavior of polymers,

**Table 6**

<table>
<thead>
<tr>
<th>Rate (°C/min)</th>
<th>$T_0$ (°C)</th>
<th>$T_e$ (°C)</th>
<th>$T_p$ (°C)</th>
<th>$t_{\text{max}}$ (min)</th>
<th>$t_{1/2}$ (min)</th>
<th>$\Delta H_c$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>153.5</td>
<td>139.2</td>
<td>149.5</td>
<td>0.78</td>
<td>0.90</td>
<td>33.4</td>
</tr>
<tr>
<td>7.5</td>
<td>152.9</td>
<td>136.2</td>
<td>148.2</td>
<td>0.61</td>
<td>0.68</td>
<td>33.2</td>
</tr>
<tr>
<td>10</td>
<td>152.6</td>
<td>134.1</td>
<td>147.5</td>
<td>0.50</td>
<td>0.57</td>
<td>33.5</td>
</tr>
<tr>
<td>15</td>
<td>152.2</td>
<td>132.0</td>
<td>146.4</td>
<td>0.36</td>
<td>0.40</td>
<td>34.9</td>
</tr>
<tr>
<td>20</td>
<td>152.0</td>
<td>127.0</td>
<td>144.2</td>
<td>0.27</td>
<td>0.37</td>
<td>33.9</td>
</tr>
</tbody>
</table>

Fig. 8. Representative polarized optical micrographs of pure sPB (a) and sPB/clay (2%) isothermally crystallized at 148 °C, respectively.

Fig. 9. Heat flow curves of sPB/clay (2%) under nonisothermal crystallization processes at indicated cooling rates.
it has also been applied directly to describe the non-isothermal crystallization of polymers. Using Eq. (1) in double logarithmic form and plotting $\log\{\ln(1/C_0)X_t\}$ versus $\log t$ for each cooling rate, the curves are shown in Fig. 11. This non-linearity of the plots indicates that the mode of spherulitic nucleation and growth is more complex than that in the isothermal crystallization process for sPB/organoclay (2%) nanocomposite and the Avrami exponent and crystallization mechanism depends on the temperature even in the early stages. All plots shown in Fig. 12 exhibit three-regimes behavior, with slope of regime 2 being much larger than those regimes 1 and 3. The regimes 1 and 2 correspond to primary crystallization, whereas regime 3, which usually proceeds over much longer time, is attributed to the occurrence of secondary crystallization. This also indicates that secondary crystallization, often occurring under isothermal crystallization, also occurs under nonisothermal crystallization. If contrasting primary crystallization under isothermal crystallization with that under nonisothermal crystallization, the conditions under nonisothermal crystallization are more complex. The kinetic parameters obtained are summarized in Table 7. For primary crystallization, the values of Avrami exponent $n_{p1}$ in the regime 1 range from 2.71 to 3.04, which indicate that, in all cases, crystallization is initiated by an athermal nucleation and proceeds with three-dimensional spherulite growth. This process occurs at higher temperatures and the results are in accordance with the primary crystallization mechanism under isothermal crystallization (as indicated in Tables 3 and 4). The values of Avrami exponent $n_{p2}$ in regime 2 vary from 3.29 to 4.71, which indicates that as the crystallization time is prolonged and the crystallization temperature decreases, the spherulites become branched, and may lead to dendrite formation. Thus, a crystal in this regime grows in a higher dimension. At secondary crystallization, the values of $n_s$ range from 1.39 to 1.98, suggesting that, in the later stage, the crystals impinge and crowd; the growth geometry of the crystal is then

Fig. 10. The relative crystallinity as a function of temperature for the nonisothermal melt crystallization of spB/clay (2%) at different cooling rates.

Fig. 11. The relative crystallinity as a function of time for the nonisothermal melt crystallization of spB/clay (2%) at different cooling rates.

Fig. 12. Plots of $\log\{\ln(1-X_t)\}$ versus $\log t$ for the nonisothermal melt crystallization of spB/clay (2%) at different cooling rates.
restricted and the crystals grow in lower dimension in this regime.

Additionally, the onset temperature of the secondary crystallization, $T_d$, is lower than $T_p$ (the temperature at which the crystallization rate reaches a maximum) and the onset time of secondary crystallization, $t_d$, is higher than $t_{\text{max}}$ (the time at which the crystallization rate reaches the maximum). This is also in agreement with data from isothermal crystallization process. The rate constants in these three regimes are dependent on the cooling rate and change in the same relative way. The values of $x_p$ decrease with increasing cooling rate. It would appear that a higher cooling rate is accompanied by an increase in the mass fraction for secondary crystallization. This may be explained as follows. An increase of cooling rate leads to decrease of absolute crystallinity during primary crystallization, and thus an increase in the fraction of amorphous components between and within the spherulites. So the mass fraction for further crystallization increases with increasing cooling rate.

It should be pointed out that for the nonisothermal crystallization process of sPB/organoclay (2%), the mechanism of crystallization is relative complex. The crystallization was divided into three regimes, primary crystallization includes different crystallization mechanism. The well-known Ozawa equation [25–29], the ‘series–parallel’ Avrami equation suggested for isothermal crystallization cannot satisfactorily describe the nonisothermal crystallization process of sPB/organoclay (2%). As nonisothermal crystallization of polymer and polymer/organoclay nanocomposites has not received the same attention as the isothermal crystallization. For improving the predication of the parameters of dynamic solidification under real processing conditions, much attention in theory and experiments should be paid to the nonisothermal crystallization processes which possess different mechanisms of crystallization.

From nonisothermal crystallization experiments of DSC. The activation energy is often estimated by using the Kissinger method. Recently, Vyazovkin and Sbirrazzuoli [30–32] has suggested that the Kissinger equation is no applicable to the nonisothermal crystallization processes that occur on cooling and the differential isoconversional method of Friedman [33] can be utilized to determine the activation energy by

$$\frac{\mathrm{d}X_t}{\mathrm{d}t} = A \exp \left( -\frac{\Delta E}{RT} \right) f(X_t)$$  \hspace{1cm} (8a)

or

$$\ln \left[ \frac{\mathrm{d}X_t}{\mathrm{d}t} \right] = \ln[Af(X_t)] - \frac{\Delta E}{RT}$$ \hspace{1cm} (8b)

where $X_t$ is the relative crystallinity, $t$ is the time, $A$ is the pre-exponential factor, and $f(X_t)$ is the crystallization model. At a fixed relative crystallinity, the slope of fitting linear on the plot of $\ln[\mathrm{d}X_t/\mathrm{d}t]$ versus $1/T$ can be obtained to be $\Delta E/R$. The values of the activation energy $\Delta E$ (shown in Fig. 13) for sPB/organoclay (2%) nanocomposites are changed with the increase of the relative crystallinity from $-307.8$ kJ/mol to $-199$ kJ/mol. In the literature, Ren et al. [7] have obtained the activation energy of a pristine sPB, ranging from $-208$ to $-142$ kJ/mol, based on Friedman method. We have also

![Fig. 13. The activation energy of crystallization as a function of relative crystallinity for sPB/clay (2%) obtained from DSC data.](image-url)
obtained the activation energy of pristine sPB [6], ranging from \(-83\) to \(-92\) kJ/mol, based on Friedman method.

6. Conclusions

A series of sPB/organoclay nanocomposites with different clay loadings have been prepared by first in situ vacuum distillation of toluene solutions and then melt-pressed, followed by characterization by DSC, TGA, POM and XRD. The XRD shows that exfoliated nanocomposites are formed in the majority at lower clay concentrations (less than 2%), at higher clay contents intercalated nanocomposites dominate. At the same time, the XRD indicates that the crystal structure of the sPB/organoclay nanocomposites do not change, only the relative intensity variation of the peaks corresponding to (010) and (200)/(110) crystal planes, respectively, was observed. The POM and DSC indicate that organoclay layers can improve cooling crystallization temperature, crystallization rate and reducing the spherulite sizes of sPB. TGA shows that under argon flow the nanocomposites exhibit slight decrease of thermal stability, while under oxygen flow the resistance of oxidation and thermal stability of sPB/organoclay nanocomposites were significantly improved relative to pristine sPB. The primary and secondary crystallization for pristine sPB and sPB/organoclay (2%) nanocomposites were analyzed based on different approaches. The nanocomposites exhibit smaller Avrami exponent and larger crystallization rate constant, with respect to pristine sPB. Primary crystallization under isothermal conditions displays both athermal nucleation and three-dimensional spherulite growth and under nonisothermal processes, the mechanism of primary crystallization becomes very complex. Secondary crystallization shows a lower-dimension crystal growth geometry for both isothermal and nonisothermal conditions. The activation energy of crystallization of sPB and sPB/organoclay nanocomposites under isothermal and nonisothermal conditions were also calculated based on different approaches.

Acknowledgements

The authors express their acknowledgment to the National Natural Scientific Fund of China (No. 20274046) and thanks to Prof. S.A. Xu of East China University of Science and Technology for providing the Cloisite 20A organoclay.

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