Effect of Palladium Nanoparticles on the Thermal Degradation Kinetics of $\alpha$ Crystalline Syndiotactic Polystyrene

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Abstract: Palladium (Pd) nanoparticles were incorporated into a neat s-PS by a drying process consisting of simultaneous vaporization, penetration and reduction steps of palladium (II) bis(acetylacetonato), Pd(acac)$_2$, used as a precursor. In order to characterize the crystalline structure, distribution of Pd nanoparticles, and thermal stability, wide-angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), and dynamic and isothermal thermogravimetric (TG) analyses were carried out. s-PS film with $\alpha$ crystalline form was prepared by rapid cooling the melted state and TEM observation showed that Pd nanoparticles were selectively located on the amorphous region. We also found that the Pd nanoparticles with 1.49 wt% enhanced the thermal stability of s-PS and the enhancement of thermal stability was mainly due to the hindrance of the mobility of polymer chains by the Pd nanoparticles.

Keywords: Pd nanoparticles, s-PS, thermal degradation, Kissinger equation

Introduction

Since syndiotactic polystyrene (s-PS) was synthesized in the late 1980s, many efforts have been done to characterize the polymorphic behaviors of this polymers and to put its impressive material properties, such as high melting temperature ($\sim 270 ^\circ$C), relatively high crystallization rate, excellent dimensional stability, and good chemical resistance, to practical use [1,2]. s-PS shows complex polymorphic behaviors of four types of the crystalline form ($\alpha$, $\beta$, $\gamma$, and $\delta$) depending on the thermal history and/or solution treatment. Generally, $\alpha$ and $\beta$ forms are generated during the melting or cooling processes, while $\gamma$ and $\delta$ forms are related to the solvent processes [3-6].

A wide range of polymers and nano-sized inorganic fillers have been combined to form nanocomposites exhibiting remarkably novel and useful properties different from the host polymers or conventional composites because of the high surface-to-bulk ratio of the fillers, resulting in the drastic increase in the interface between the polymers and the fillers. Uniformly dispersed metal nanoparticles offer strong possibility of fabricating functional materials with useful catalytic [7], optical [8], sensing [9], magnetic [10], or electrical [11] properties. Therefore many researchers have devoted to the development of new polymer/metal hybrid materials and to the prediction of their final properties. The fabrication methods can mainly be classified into five: (1) a metallic precursor dissolved with a polymer in a solvent is reduced to the metallic nanoparticles during stirring, heating and evaporating solvent; (2) a metallic precursor is dissolved in a monomer and is reduced to the metallic nanoparticles during the polymerization; (3) a colloid of metal nanoparticles prepared by a pretreatment is mixed with a polymer solution or monomers being followed by the similar procedure of (2) or (3); (4) a polymer matrix is impregnated with a solvent containing metal precursor and treated by reduction agents or by thermolysis; and (5) a sublimed metallic precursor penetrates into the polymer film and is reduced to self-assembled metallic nanoparticles, which was developed by our group [12-14].
In this paper, the form crystalline structure was prepared by controlling the cooling rate from the molten state of s-PS and palladium (Pd) nanoparticles were incorporated into the film by our drying process [14]. Then, we studied the thermal degradation kinetics in order to know how the loaded Pd nanoparticles enhance the thermal stability of the s-PS.

**Experimental**

Palladium(II) bis(acetylacetonato), Pd(acac)_2, was purchased from Johnson Matthey Materials Technology and were recrystallized from acetone before use. s-PS (> 90% syndiotactic, Mw: 250,000, Tm: ~273 °C) was from Polymer Source Inc. and as-received s-PS was dried at 60 °C for 48 hr in vacuum oven. 100 µm thick film with α-crystalline form was prepared by compression molding preheated at 300 °C for 10 min and cooled quickly to 220 °C at a cooling rate of 40 °C/min. Then, it was maintained for 30 min and cooled to room temperature at a cooling rate of 1 °C/min.

Pd loading was carried out through the following procedure: 10 mg of Pd(acac)_2 in the glass tube reactor was sublimed at 180 °C in vacuo and condensed on the upper side of the glass wall. Then the s-PS film was placed into the reactor and maintained at 180 °C of N2 atmosphere for (a) 0 min, (b) 30 min, (c) 60 min, and (d) 120 min in the free-standing state. To avoid the annealing effect due to the different incorporation time, all samples were annealed at 180 °C for the rest time to be totally 120 min without Pd(acac)_2 vapor condition.

To study the thermal degradation characteristics of the s-PS/Pd nanocomposites, thermogravimetry (TG), (TG/DTA 6200, EXTRA 6000 series, Seiko Instruments Inc.) was employed at the nitrogen flow rate of 200 mL/min to prevent the oxidation of the composites. The shapes of the samples were of film chip and the sample weight was 3–4 mg. Dynamic run was carried out from room temperature to 600 °C at the heating rates of 5, 10, 15, and 20 °C/min, and isothermal run was done at 360 °C. Derivative thermogravimetry (DTG) curve, that is, weight loss rate curve was calculated from the TG curve.

The incorporated Pd content was estimated by measuring % char yield after carrying out thermolyze the s-PS/Pd nanocomposites at 800 °C for 1 hr in the electric furnace with Ar condition.

Wide-angle X-ray diffraction (WAXD) patterns were measured by a diffractometer (Rigaku Directx 8000) operated at 40 kV and 100 mA with copper filtered CuKα radiation at a scanning rate of 1.0 °/min using the film state samples.

Transmission electron microscopy (TEM) employed with a LEO922 energy-filtering transmission electron microscope (LEO Elektronenmikroskopie GmbH, Germany) at an accelerating voltage of 200 kV. Thin sections for TEM observation were prepared by cryo-ultramicrotomy at -60 °C after embedding in a light curable resin (D-800, JEOL DATUM), and then the sections were stained with the vapor of RuO4 for 10 min.
Results and Discussion

WAXD analysis verifies that the neat s-PS and s-PS/Pd systems are consisted of 100 % α form, as shown in Figure 1A. Speaking in detail, α′ modification peaks are present at 2θ = 6.7, 11.8, 13.5, and 20.4° without α″ modification in the (a) pattern for neat s-PS however, when Pd nanoparticles are incorporated into the (a) sample at 180 °C, two new peaks at 2θ = 15.6 and 18.0° and a new shoulder at 2θ = 14.1° appear, and a very weak peak is also newly shown at 2θ = 10.3°, as was displayed on the spectra (b), (c), and (d) in Figure 1A. These four additional peaks characterize the α″ modification [3]. The intensities of the disordered α′ modification and the ordered α″ modification increase slightly with increasing Pd incorporation time, that is, with increasing Pd content, where the Pd contents for the samples (b), (c), and (d) are 1.49, 2.13, and 2.52 wt%, which were estimated by measuring % char yield after carrying out thermolyze the s-PS/Pd systems at 800 °C for 1 hr in the electric furnace with Ar condition.

Figure 1B shows TEM micrograph of lamellae microstructure for the sample (c), which was acquired with the stained specimens with RuO₄ and the inset shows the Pd nanoparticles acquired with the unstained specimen. The
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Table 1. The Relationship between Heating Rate (q) and Maximum Weight Loss Temperature (T_p) for the Neat s-PS

<table>
<thead>
<tr>
<th>q (K/min)</th>
<th>T_p (K)</th>
<th>-ln(q/T_p^2)</th>
<th>1/T_p × 10^3 (K^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>401.0</td>
<td>11.42</td>
<td>1.48</td>
</tr>
<tr>
<td>10</td>
<td>411.4</td>
<td>10.75</td>
<td>1.46</td>
</tr>
<tr>
<td>15</td>
<td>419.9</td>
<td>10.37</td>
<td>1.44</td>
</tr>
<tr>
<td>20</td>
<td>423.9</td>
<td>10.10</td>
<td>1.43</td>
</tr>
</tbody>
</table>

Figure 4. Kissinger plot for the calculation of thermal degradation kinetic parameters of the neat s-PS.

staining with RuO_4 can visualize the lamellae morphologies, where the amorphous (dark) regions that are formed by tie molecules jointing the lamellae (bright) are selectively stained and Pd nanoparticles (black dots) with the average diameter of about 5.4 nm are also selectively on the amorphous regions.

Figure 2 presents the TG curves for s-PS films exposed to the Pd(acac)2 vapor for (a) 0, (b) 30, (c) 60, and (d) 120 min in dynamic (left-hand side) and isothermal (right-hand side) runs. In the dynamic TG analysis carried out at 10 °C/min, neat s-PS begins to exhibit significant weight loss at about 330 °C and almost all s-PS polymer chains degrade in one stage between 330 ~ 440 °C. The onset of the thermal degradation of the sample (c) is shifted to higher with about 30 °C and almost all weight loss is exhibited in the range of 360 ~ 445 °C. It means Pd nanoparticles improve the thermal stability of s-PS. The thermal degradation scheme of PS chains involves the initiation of free radicals, the propagation via chain transfer and first-order termination [15]. In the isothermal TG curves at 360 °C which is close to the onset temperature of the degradation, 1.49 wt% Pd nanoparticles strongly improve the thermal stability showing the times for which 50 wt% of s-PS losses (T_τ) is about 2.3 times longer than that of neat s-PS. However, too much incorporation of Pd nanoparticles decreases the effect on the thermal stability.

To study the effect of Pd nanoparticles on the kinetic parameters for the thermal degradation, the following

Table 2. Thermal Degradation Kinetic Parameters for s-PS/Pd Nanocomposites Estimated by Kissinger Equation

<table>
<thead>
<tr>
<th>Pd Content (wt%)</th>
<th>Activation Energy, Ea (kJ/mol)</th>
<th>Pre-exponential Factor, A (sec^-1)</th>
<th>Rate Constant, k at 360 °C (sec^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>219.5</td>
<td>5.2 × 10^14</td>
<td>4.0 × 10^-4</td>
</tr>
<tr>
<td>1.49</td>
<td>214.5</td>
<td>5.1 × 10^13</td>
<td>1.0 × 10^-3</td>
</tr>
<tr>
<td>2.13</td>
<td>211.8</td>
<td>4.8 × 10^13</td>
<td>1.6 × 10^-4</td>
</tr>
<tr>
<td>2.52</td>
<td>207.2</td>
<td>4.7 × 10^13</td>
<td>3.7 × 10^-3</td>
</tr>
</tbody>
</table>

Figure 5. (A) DTG curves for s-PS/Pd (1.49 wt%) nanocomposite and (B) the Kissinger plot for the calculation of thermal degradation kinetic parameters.
Kissinger expression was adopted [16,17].

\[ \ln \frac{q}{T_p^2} = \frac{E_a}{RT_p} - \ln \frac{AR}{E_a} \]

where q: heating rate, \( T_p \): the temperature at which the maximum weight loss rate appeared, \( E_a \): thermal degradation activation energy, \( R \): gas constant, 8.314 J/mol-K and \( A \): pre-exponential factor.

Figure 3A was acquired from the dynamic TG analysis for the neat s-PS carried out at four different heating rates and they were differentiated to get experimental \( T_p \) values of each heating rate on the derivative thermogravimetry (DTG) curves, as shown in Figure 3B. To use Kissinger equation, two variables \( -\ln (q/T_p^2) \) and \( 1/T_p \) were calculated from the DTG curves and they were listed on Table 1. The linear relationship between \( -\ln (q/T_p^2) \) and \( 1/T_p \) was plotted in Figure 4 in order to estimate an activation energy and a pre-exponential factor. The former was calculated from the slope and the latter was from the y-intersection and the linear relationship between \( -\ln (q/T_p^2) \) and \( 1/T_p \) for the neat s-PS was \( -\ln (q/T_p^2)=26.4\times10^3/(1/T_p)-27.8 \), therefore the activation energy and pre-exponential factor for the thermal degradation were 219.5 kJ/mol and 5.2×10^{14} \text{ sec}^{-1}, respectively.

Figure 5A shows DTG curves derived from TG curves for s-PS/Pd (1.49 wt%) system. Polymer chains were degraded in one stage regardless of heating rate and two variables \( -\ln (q/T_p^2) \) and \( 1/T_p \) were calculated from the DTG curves. Kissinger plot was displayed on Figure 5B giving the expression, \( -\ln (q/T_p^2)=25.8\times10^3/(1/T_p)-25.5 \), therefore activation energy and pre-exponential factor were 214.5 kJ/mol and 5.1×10^{13} \text{ sec}^{-1}, respectively.

Thermal degradation of polymer chains in the s-PS/Pd nanocomposites took place in one stage regardless of Pd content. Using the Kissinger equation, the kinetic parameters for the s-PS/Pd nanocomposites with various Pd contents were obtained and they were listed on Table 2. The activation energy slightly decreased with increasing Pd content, while pre-exponential factor for s-PS/Pd (1.49 wt%) nanocomposite was 10 times lower than that for neat s-PS and then slightly decreased with increasing Pd content. It has been well known that the decrement of pre-exponential factor enhances the thermal stability of polymer chains however the decrement of activation energy is harmful to that. These results suggest that the enhancement of the thermal stability is attributed to the decrease in the pre-exponential factor. That is, the collision frequency of the polymer chains largely decreases, suggesting that the mobility of the polymer chains is suppressed due to the hindrance by the Pd nanoparticles. It has been well known that the thermal degradation PS chains begins with the formation of free radicals by unzipping initiated by random scission, and then they transfer to adjacent chains via intermolecular and intramolecular chain reactions followed by termination step [15]. Thus, it indicates that the Pd nanoparticles have an ability to suppress the chain transfer reaction.

To compare thermal degradation rate for the four systems, each activation energy and pre-exponential factor is introduced to the following Arrhenius equation to get rate constants at a selected temperature and the data are also shown in Table 2.

\[ k = A \exp \left( \frac{E_a}{RT} \right) \]

where \( k \) is the rate constant and \( T \) is a selected temperature (360 °C). The rate constant for s-PS/Pd (1.49 wt%) nanocomposite is 4 times lower than that for neat s-PS and this result is well agreed with the isothermal TGA data of Figure 2.

**Conclusions**

s-PS/Pd nanocomposites were produced by incorporation of vaporized palladium precursor into crystalline s-PS film with solid state in our drying process. The precursors were penetrated into the amorphous region and they simultaneously reduced to Pd metallic nanoparticles so that Pd nanoparticles were selectively located on the amorphous regions that are formed by tie molecules jointing the crystalline lamellae. In the WAXD patterns, the intensities of the disordered \( \alpha' \) and ordered \( \alpha'' \) modifications increase slightly with increasing Pd content. Pd nanoparticles enhanced the thermal stability of s-PS and the enhancement of thermal stability was mainly due to the hindrance of the mobility of polymer chains by the Pd nanoparticles. As 1.49 wt% of Pd nanoparticles were incorporated, the thermal stability was 4 times modified.

**References**

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