Crystallization Studies of Poly(trimethylene terephthalate)/Silica Nanocomposites Prepared by Sol–Gel Technique

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ABSTRACT: Poly(trimethylene terephthalate) (PTT)/silica nanocomposite films were successfully fabricated using a novel sol–gel approach. The synthesis of these nanocomposites is being carried out by hydrolysis and condensation of tetraethoxysilane using trifluoroacetic acid with a small amount of water. The scanning electron microscopy and zetasizer result showed that the silica particles with a size range of 80−100 nm were homogeneously dispersed in the PTT matrix. The effect of different amounts of silica on crystallization of PTT was investigated using X-ray diffraction, differential scanning calorimetry (DSC), and optical microscopy. Polarized light microscopic results revealed that the spherulite size gradually decreased with increasing silica loading and increased with crystallization temperature for a given nanocomposite during isothermal melt crystallization. PTT with a small amount of SiO2 melt crystallized at low temperatures showed banded spherulites. DSC results revealed that nonisothermal cold crystallization temperature decreased with silica content, whereas no significant change in nonisothermal melt crystallization behavior was observed with silica content. The crystallinity of isothermally melt crystallized PTT increased with both crystallization temperature and silica loading.

1. INTRODUCTION

Poly(trimethylene terephthalate) (PTT) is an aromatic polyester with three methylene groups in the glycol unit joining other aromatic polyesters such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). PTT has better elastic recovery and low modulus than PET, PBT, and polyamide 6, and it is an ideal candidate for soft and stretchable fibers.1−5 PTT was first synthesized in 1941 using propane diol and dimethyl terephthalate. It was not commercially available until 1998 due to the cost of propane diol. DuPont and Shell Chemical introduced new ways to make propane diol that leads to the commercialization of PTT and fundamental research of PTT. PTT has also been used in optical communications, optical data processing, and nonlinear optics. Melt crystallization and cold crystallization of PTT have been investigated, and conformational and morphological changes during crystallization were conducted by Fourier transform infrared (FTIR) spectroscopy and optical microscopy.6−11

Polymer nanocomposites derived from nanoscale additives and polymer matrix became interesting new type of composite materials. Several methods such as melt blending, intercalation, and in situ intercalative polymerization have been used for the preparation of these nanocomposites.12−20 Among them, montmorillonite clay,12−19 carbon nanotubes,20 and SiO2 nanoparticles21−28 are commonly used as nanofillers. The crystallization behavior of semicrystalline polymers in the presence of nanofillers has been investigated extensively;29−35 and studies have shown that nanoparticles can influence the flow, crystallization, and the final morphology of the polymer. The characteristics of polymer nanocomposites depend on the type of interaction between nanoparticles and the polymer matrix.36−39 It has been demonstrated that dispersion of nanoparticles plays a significant role in mechanical, physical, and crystallization behavior of polymer nanocomposites.

The polymer/silica nanocomposites were prepared recently by the in situ sol–gel reactions.33−40 It has been shown that silica derived from silicon precursors enhance physical and mechanical properties of polymers. The sol–gel syntheses of organic–inorganic nanocomposites are being carried out using silane-coupling agents such as alkoxyl silanes as precursors. Alkoxy groups hydrolyze during sol–gel process in the presence of water and form cross-link network. PTT/silica nanocomposite was prepared via the sol–gel technique and in situ polymerization.35 It has been shown that PTT chains were grafted on the surface of silica. PTT nanocomposite prepared by this technique showed high mechanical properties. This study reports the synthesis of PTT/silica nanocomposites using an in situ sol–gel process using PTT and tetraethoxysilane (TEOS). The effect of silica on isothermal and nonisothermal melt crystallization of PTT was investigated. The novelty of this work lies on that the silica nanoparticles were created within the PTT phase for the first time using the solvent for PTT.
2. RESULTS AND DISCUSSION

2.1. Characterization of PTT Nanocomposites. The sol–gel method is an efficient method to prepare inorganic networks. It offers several advantages such as controlling particle size by optimizing conditions such as pH, concentration, and temperature. In the present study, PTT/silica nanocomposites with varying amount of TEOS (1–10 wt %) were fabricated using the sol–gel technique by adding silica precursor to PTT trifluoroacetic acid solution contained 10 wt % water. The dispersion of silica particles in the PTT matrix was determined to understand the physical and mechanical properties and morphology of PTT nanocomposites. Figure 1 illustrates scanning electron microscopy (SEM) images of PTT nanocomposites containing 5 wt % TEOS by weight at two different magnifications along with SEM image of PTT nanocomposites containing 10 wt % TEOS by weight. These SEM micrographs clearly show that nanoscale spherical silica particles were homogenously distributed within the PTT matrix. However, SEM image of PTT containing 10 wt % TEOS shows aggregation of SiO2 nanoparticles. Silica particle size of 80–100 nm was determined using SEM. The effect of silica loading on polymer molecular weight was investigated using viscosity measurement using trifluoroacetic acid as solvent. No significant change in molecular weight was observed. PTT/silica nanocomposites were recently prepared by the traditional two-stage melt poly-condensation method.26 It was shown by FTIR and NMR spectroscopy that PTT chains were grafted on the surface of silica particles. It was also reported that molecular weight of PTT gradually decreased with increasing silica content. The decrease in viscosity average molecular weight was attributed to the small amount of ethanol produced during polymerization.

The size of the prepared silica particles was further determined using zetasizer instrument. To determine the size of the SiO2 particles, PTT nanocomposites films were dissolved in trifluoroacetic acid and filtered through the membrane filter to separate SiO2 particles from the polymer. Silica particles were then suspended in a solvent and stirred for 30 min. The average size of the particles was determined as 80 nm, shown in Figure 2. It is in good agreement with our SEM images. Figure 1. SEM images of PTT nanocomposite with 5 wt % TEOS at two different magnifications (a, b) and PTT nanocomposite with 10 wt % TEOS (c).

Figure 2. Particle size analysis report of the silica particles stirred for 3 h.
findings. These PTT nanocomposite films were then characterized by X-ray diffraction (XRD). The presence of SiO₂ particles within the PTT polymer matrix was not confirmed by XRD. XRD pattern of neat SiO₂ shows a broad reflection at \( \sim 2\theta = 25 \), suggesting amorphous phase of silica. It was absent in the XRD pattern of PTT nanocomposites due to low concentration.

The effect of the nanoparticles on the crystal structure of PTT was further investigated by XRD. A single crystal form has been identified for PTT.40−42 The unit cell of this crystal form was identified as triclinic, with \( a = 4.637, b = 6.226, c = 18.64 \, \text{Å}, \alpha = 98.4^\circ, \beta = 93^\circ, \) and \( \gamma = 111.5^\circ \). The XRD results showed that PTT crystal form is not affected by the presence of nanoparticles, but a significant change in crystallinity of PTT nanocomposite compared to neat PTT was observed.

2.2. Crystallization Studies of PTT/SiO₂ Nanocomposite by Optical Microscopy. The effect of silica on morphology of melt crystallized pure PTT and its nanocomposites was studied by optical microscopy. It is clear from optical micrographs that both the melt crystallization temperature and the silica content influence the morphology of melt crystallized PTT. Figure 3 shows the optical micrographs of PTT/SiO₂ nanocomposite melt crystallized at 120, 150, and 180 °C for 30 min. Optical micrograph of neat PTT crystallized at 120 °C shows a well-defined spherulite morphology without banded structures roughly about 200 microns. In contrast, a significantly different morphology was observed for PTT with 1 and 2 wt % TEOS. Spherulites with banded structures are seen for PTT nanocomposites with 1 and 2 wt % TEOS, and these banded structures disappeared when the TEOS content increased more than 2%. Figure 3A clearly shows that the spherulite size decreases with increasing TEOS content, suggesting heterogeneous nucleation in the presence of silica. As a result, the number of spherulites increased with increasing silica content. Similar observation was made for PTT nanocomposites crystallized at 150 and 180 °C, but there were no banded structures observed at these crystallization temperatures.

Effect of melt crystallization temperature on spherulitic morphology of PTT was studied previously.5,43,44 It was apparent that spherulite size increased with increasing crystallization temperature for both neat PTT and PTT nanocomposites. Figure 4 displays PTT with 5 wt % TEOS melt crystallized at 120, 150, and 180 °C for 30 min. The orientation of the crystalline lamella along or perpendicular to the spherulite radius is evident from Maltese cross pattern. It can also be seen that the spherulite size increases with increasing melt crystallization temperature, indicating a slower crystallization rate at higher temperature.18 The spherulite size of melt crystallized PTT nanocomposite with 5 wt % TEOS at 120 to 150 to 180 °C increases from about 50 to 70 to 100 μm, respectively. It was observed that the introduction of higher loadings of silica at higher melt crystallization temperatures forms smaller spherulites. This suggests that silica particles act as nucleating agent and form larger number of nuclei. Since larger number of nuclei forms simultaneously within a limited space, spherulites grow smaller.

PTT crystallized from the melt was studied by optical microscopy and shown that PTT exhibits three crystallization regimes I, II, III. PTT forms axialites or elliptically shaped spherulites in regime I and changes to banded and nonbanded spherulites in regime II and III, respectively.53 The banded spherulites were dominant at crystallization temperature above 195 °C (regime II) and the banded morphology disappears at crystallization temperature below 195 °C, in good agreement...
nanocomposites. In the present study, banded spherulites were seen for PTT nanocomposites with small amount of SiO2 at 120 °C. Bands in these spherulites appear to be in regular interval with dark and bright bands. It is clear that nanoparticle plays similar role as higher melt crystallization temperature due to decrease in rate of crystallization and heterogeneous nucleation.

2.3. Thermal Characterization of the PTT/Silica Nanocomposite. It is well known that the crystallization plays a significant role in the properties of polymer nanocomposites. Therefore, the effects of SiO2 on isothermal and nonisothermal melt crystallization and cold crystallization behavior of PTT nanocomposites were investigated by means of differential scanning calorimetry (DSC). Thermal properties obtained from DSC scans are listed in Table 1. The weight loss measurement of neat PTT and its nanocomposites with varying amounts of silica as a function of temperature was carried out using thermogravimetric analysis to determine thermal stability. The amount silica determined in each PTT nanocomposite is also given in Table 1. The DSC curves of amorphous PTT and PTT nanocomposite films nonisothermally cold crystallized at a heating rate of 10 °C/min are depicted in Figure 5a. The melting curve of nonisothermally cold-crystallized PTT/SiO2 nanocomposites is shown in Figure 5b.

The DSC scan of neat PTT amorphous film in Figure 5a showed two transitions that were attributed to glass-transition temperature (Tg at 45 °C) and a cold crystallization temperature (Tcc at 56 °C). The Tg of PTT nanocomposites is not seen in their DSC scans, suggesting that the incorporation of nanoparticles in the PTT matrix does influence the Tg of PTT. The Tcc of PTT nanocomposites was observed at lower temperatures compared to neat PTT, and the Tcc appeared to decrease with the increasing SiO2 content. For example, the Tcc is shifted to 46 °C for PTT nanocomposite with 1% TEOS, and the Tcc is shifted to 41 °C for PTT nanocomposite with 10% TEOS. The heat of nonisothermal cold crystallization exotherm (ΔHcc) of neat PTT is found to be 30.0 J/g whereas the ΔHcc of PTT nanocomposite with 10% TEOS is found to be 17.0 J/g. It is clear that the ΔHcc decreases with TEOS loading. This is probably due to inability of PTT chains to be incorporated within the crystals because of faster cold crystallization rate. Similar studies were conducted for PTT/clay nanocomposites to show the effect of clay on morphology of PTT. It was shown that the Tcc increased with increasing clay content, suggesting lower crystallization rate. The decrease in crystallization rate with addition of clay in PTT nanocomposites was attributed to the interaction between the PTT chain and clay preventing the mobility of the PTT chains. A slight increase in the melting temperature (Tm) of PTT with the increasing TEOS content was observed.

Nonisothermal melt crystallization of PTT and its nanocomposites with different TEOS loadings was investigated at a cooling rate of 10 °C/min. Figure 6 shows the DSC cooling curves of PTT nanocomposites from the melt. In the case of neat PTT, nonisothermal melt crystallization peak, Tc, appears around 202 °C; however, Tc shifts to slightly lower temperature in the presence of SiO2. Finally, isothermal melt crystallization of PTT nanocomposites was carried out at 120, 150, and 180 °C in an oven for 30 min. Figure 7 shows the DSC heating scans of PTT nanocomposites with varying

**Table 1. DSC Data of Neat PTT and Its Nanocomposites Derived from First Heating Scans**

| sample          | SiO2 content (wt %) | Tg (°C) | Tcc (°C) | ΔHcc (J/g) |
|-----------------|---------------------|---------|----------|------------|
| PTT             | 0                   | 56      | 217      | 30         |
| PTT/3%TEOS      | 0.9                 | 46      | 218      | 25         |
| PTT/5%TEOS      | 1.4                 | 41      | 219      | 19         |
| PTT/10%TEOS     | 2.5                 | 42      | 218      | 17         |

**Figure 4.** Optical micrographs of PTT nanocomposite with 5% TEOS melt crystallized at (a) 120 °C, (b) 150 °C, (c) 180 °C.
amounts of TEOS melt crystallized at 150 °C, and similar patterns were observed for PTT nanocomposites melt crystallized at 120 and 180 °C. It is clear from the Figure 7 that the melting temperature of PTT increased with increasing SiO₂ content at all melt crystallization temperatures studied. Melting endotherm shows two peaks, and they are attributed to bimodal distribution of crystallites. The increase in melting temperature with silica content is attributed to lamella thickness increase due to increase in crystallinity. Figure 8 shows the crystallinity of PTT nanocomposites melt crystallized at different temperatures (120, 150, and 190 °C) for 30 min. Crystallinity (χc) values for pure PTT and its nanocomposites were determined using the heat of fusion (ΔHf) value of 100% crystalline PTT. It should be noted that the heat of fusion of a perfect PTT crystal was multiplied by the fraction of PTT in each sample. The crystallinity values increased slowly with crystallization temperature (Tc), whereas the crystalline fraction (χc) increased rapidly with the increasing SiO₂ content, indicating that PTT crystallizes more in the presence of SiO₂.

3. CONCLUSIONS

PTT/SiO₂ nanocomposites were synthesized via the novel sol–gel reaction between TEOS and PTT. X-ray diffraction
and scanning electron microscopy techniques revealed the formation of these nanocomposites. It was found that the size of the silica nanoparticles in the PTT matrix was about 80–100 nm. SEM results confirmed that the dispersion of nanoparticles is uniform up to 5% silica content, and nonuniform dispersion was apparent for those containing more than 5% silica content.

The introduction of silica nanoparticles on crystallization behavior of PTT nanocomposite was investigated using DSC. Crystallinity of PTT nanocomposites increased with TEOS content compared to neat PTT. It was found that the size of the spherulites depends on the crystallization temperature as well as the silica content. The spherulite size increased when the crystallization temperature increased from 120 to 180 °C, whereas the spherulite size decreased with increasing TEOS content at a given crystallization temperature, suggesting that the addition of silica modifies the crystallization behavior of PTT.

4. EXPERIMENTAL SECTION

4.1. Materials. Poly(trimethylene terephthalate) pellets with weight and the number average molecular weight about 78 000 and 34 000 g/mol, respectively, were received from DuPont, and its viscosity of 0.85 dL/g was measured in dichloroacetic acid at 23 °C. The molecular weight distribution was approximately 2.0. Tetraethoxysilane (TEOS) and trifluoroacetic acid at 23 °C were purchased from Sigma-Aldrich Inc. All of the chemicals were used without further purification.

4.2. Preparation of Polymer/Silica Nanocomposite. PTT pellets (0.5 g) were placed in a beaker, and 36.0 mL of trifluoroacetic acid and 4.0 mL of water were added. The pellets were dissolved at low temperature with continuous stirring until the pellets were dissolved completely. Once all of the pellets were dissolved, amounts of 10, 5, 4, 3, 2, and 1 wt % tetraethoxysilane (TEOS) were added and stirred until the solution becomes clear. The solution was allowed to dry for about 24 h at room temperature. After 24 h, the fully dried samples were triturated to fine powder using mortar and pestle and stored in the desiccator.

Neat PTT and PTT nanocomposites amorphous films were prepared using following procedure: 0.158 g of fine powder was sandwiched between two Teflon sheets and melt pressed at 260 °C and held 10 000 lb pressure for 5 min and subsequently transferred to an oven preheated to the desired crystallization temperatures (T_c): 120–180 °C for 30 min for crystallization.

4.3. Differential Scanning Calorimetry. Thermal properties of neat PTT and PTT/silica nanocomposites were measured using a TA Instruments Differential Scanning Calorimeter Q2000. Indium and zinc standards were employed for temperature and heat of fusion calibration. The glass-transition temperature, melting temperature, and cold crystallization temperature of melt crystallized PTT and its nanocomposites crystallized at various temperatures were obtained by heating the sample from 30 to 250 °C at a rate of 10 °C/min. Nonisothermal melt crystallization of PTT nanocomposites was carried out by heating from 30 to 260 °C at a heating rate of 10 °C/min, held at 260 °C for 5 min, and then cooled from 260 to 25 °C at a cooling rate of 10 °C/min. Nonisothermal cold crystallization of PTT nanocomposites was carried out by heating from 30 to 260 °C at a heating rate of 10 °C/min. 3–5 mg was used and onset values were taken as melting, cold crystallization, and nonisothermal melt crystallization temperatures. Integration of melting peak was carried out between 195 and 235 °C to determine heat of fusion. The crystalline fraction was determined using the equation below.

\[ \text{Crystallinity} = \frac{(\Delta H_{m} - \Delta H_{c})}{\Delta H_{m}} \]

Where \( \Delta H_m \) is heat of fusion of the sample, \( \Delta H_c \) is heat of cold crystallization, and \( \Delta H_{m} \) is heat of fusion of 100% crystalline polymer and x is the wt % TEOS. Heat of fusion of 100% crystalline polymer PTT was taken as 145.63 J/g.

4.4. Microscopy. Morphology of melt crystallized PTT and PTT nanocomposite films was examined using a Nikon polarized optical microscope equipped with a 35 mm Minolta X-700 camera. PTT nanocomposite film samples were prepared by placing a piece of film between a glass slide and cover slip. The spot advanced program was used to take all photographs and measurements of the samples. Scanning electron microscopy images were examined using a field-emission scanning electron microscope with Oxford EDS Detector (FESEM-EDS) using a 5 kV accelerating voltage at New Jersey Institute of Technology. Images were recorded from the surface of cry-fractured samples coated with silver for enhanced conductivity.

4.5. X-ray Diffraction (XRD). XRD scans of PTT nanocomposites were obtained at room temperature using the Scintag X1 Advanced Diffraction System equipped with Ni-filtered Cu Kα radiation as a source of radiation. The copper anode generates a desired radiation of 1.54 Å, and the samples were scanned at room temperature from 5 to 60° at the rate of 2.4°/min with a step size of 0.020°.

4.6. Zeta Seizer Analysis. Malvern zeta seizer was used to analyze the samples for the size of the particles. About 1 mL of nanosuspension was placed in a vial and inserted into the slot for measurement in zeta seizer. It works on the principle of dynamic light scattering technique. It is an ideal technique for measurement of size of nanoparticles without perturbation for convenient size analysis. Dynamic light scattering works on the principle that particles in solution are in constant thermal fluctuate at a particular angle, which is detected by a photodiode array detector. Intensity changes are given as a correlation function, which provide size and size distribution.

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Notes
The authors declare no competing financial interest.

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