Synthesis of nano-sized \( \text{TiO}_2/\text{poly(AA-co-MMA)} \) composites by heterocoagulation and blending with PET

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Abstract

Nano-sized \( \text{TiO}_2 \) or \( \text{SiO}_2/\text{TiO}_2 \) particles were prepared by hydrolysis and condensation reactions in aqueous media, followed by mixing with poly(AA-co-MMA) latex to form different composites, then blending with poly(ethylene terephthalate), PET. The TGA results of composites indicated that negative charged latexes had greater interaction with \( \text{TiO}_2/\) or \( \text{SiO}_2/\text{TiO}_2 \) particles through strong electrostatic forces, while cationic latexes incorporated with \( \text{TiO}_2 \) or \( \text{SiO}_2/\text{TiO}_2 \) particles by \( \text{pH} \)-induced coagulation, carbonyl group chelation and hydrogen bonding. The soapless latex polymer particles showed lower ability of adsorption to \( \text{TiO}_2 \) particles due to the decrease of total surface area of these larger particles. If \( \text{SiO}_2/\text{TiO}_2 \) particles were used instead of \( \text{TiO}_2 \) particles, unexpected high adsorption result was observed. Morphology results observed by SEM showed that PET blended with positive charged composites was more homogeneous than PET blended with negative charged composites. DSC results also indicated that the \( T_g \) of PET was increased, melting temperatures (\( T_m \) or \( T'_m \)) were increased, and the temperature range of crystallization was narrowed after blending with the composites. The presence of composites affected the mobility and packing of PET molecular chains therefore changing the thermal properties of PET.

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1. Introduction

In recent years, many efforts have been focused on the organic/inorganic composite materials with various compositions. By combining organic and inorganic materials, new composites can possess advantages of both organic and inorganic components, thus creating extensive applications in many areas. Among many inorganic chemicals, titanium dioxide, \( \text{TiO}_2 \), is one of the most useful inert materials, and it is non-toxic, and inexpensive in the nanocomposite synthesis. Its various applications are studied for antifouling, antimicrobial, deodorizing and photovoltaic effects [1]. For example, Peña et al. [2] studied \( \text{TiO}_2 \) reinforced hydrogels of poly(acrylic acid) and poly(methyl methacrylate) prepared by reactive molding. Iketani et al. [3] prepared \( \text{TiO}_2/\text{poly(dimethylsiloxane)} \) transparent films on PMMA substrates with various ratios. Chen et al. [4] synthesized trialkoxysilane-capped PMMA–\( \text{TiO}_2 \) thin films which are potentially useful in optical application. Anderson reported that the catalyst behavior of \( \text{TiO}_2 \) can be improved by incorporation with \( \text{SiO}_2 \) [5].

There are several ways to prepare \( \text{TiO}_2 \) or \( \text{SiO}_2 \)-based organic/inorganic composites. By in situ sol–gel reaction of \( \text{TiO}_2 \) in different polymer solutions, well-dispersed \( \text{TiO}_2 \) particles can be obtained with enhanced electro-optical, mechanical, and thermal properties [6–10]. Sondi et al. [11] created stable dispersions of nano-silica coated with tert-butyl acrylate polymer by in situ polymerization of monomer adsorbed on the particles in 2-propanol. Bourgeat-Lami and Lang [12] synthesized polymer encapsulation of small silica particles using dispersion polymerization of styrene in aqueous ethanol with PVP. Yang and Dan [13] prepared PMMA/\( \text{SiO}_2 \) composite particles via emulsion polymerization. Other methods included coupling reaction, using a coupling agent to combine organic and inorganic parts by covalent bonds, and seeded emulsion polymer-
ization [14,15], related to inorganic phase coated with a thin polymer layer in a core–shell morphology [16]. Inorganic and organic colloid can also be made into a mesoscopic structure with raspberry-like morphologies. The general process involves assemblage, by charge attraction, for example, of small particles onto larger ones.

In this paper, inorganic components, TiO$_2$ and SiO$_2$/TiO$_2$ dispersion, were prepared by acid-catalyzed sol–gel reaction, and organic components, three kinds of poly(AA-co-MMA) latexes, were synthesized by different emulsion polymerizations. By controlling the reaction conditions, inorganic particles and organic latexes were endowed with different surface charges. According to Hunter’s [17] definition of heterocoagulation, which concerned interaction between surfaces having significantly different charge status, both inorganic and organic components were mixed to create different organic/inorganic composites. The interaction between organic polymer latexes and inorganic nanoparticles was discussed. Furthermore, these TiO$_2$/latex composites or SiO$_2$/TiO$_2$/latex composites were blended with PET. The compatibility between these components was investigated. Inorganic nanoparticles and organic copolymer latexes were characterized by DLS, XRD, FT-IR, XPS, and Zeta potential measurement. Interaction between inorganic and organic components was analyzed by TGA. The morphology was observed with SEM. Effect of composites on the thermal and crystallization properties of PET were tested with DSC.

2. Materials and experiments

2.1. Materials

Titanium tetraisopropoxide (TTIP) and tetraethoxysilane (TEOS) were used to prepare inorganic particles. Concentrated nitric acid was used as a peptizer. Acrylic acid (AA) and methyl methacrylate (MMA) were used to synthesize poly(AA-co-MMA) latexes, initiated by potassium persulfate (KPS) or 2,2’-azobis(isobutyramidine) dihydrochloride (AIBA). Sodium dodecyl sulfate (SDS) and cetyltrimethylammonium chloride (CTAC) were used as anionic and cationic surfactants, respectively. All the chemicals mentioned above were purchased form Acros and used as supplied. PET powder of intrinsic viscosity $= 0.64$ was provided by China Textile Institute. Deionized water was used throughout the work.

2.2. Preparation of TiO$_2$ dispersion

TiO$_2$ dispersion was synthesized by adding 25.6 ml titanium tetraisopropoxide (TTIP) and 6 ml nitric acid into 308 ml deionized water, then refluxing at 90 $^\circ$C for 1 h. When TTIP was added to deionized water, white solid particles precipitated immediately, which then re-dissolved during the stirring and refluxing. At the end of reaction, a clear, transparent TiO$_2$ dispersion was obtained.

2.3. Preparation of SiO$_2$/TiO$_2$ dispersion

SiO$_2$/TiO$_2$ dispersion was synthesized by a sol–gel reaction of TEOS in the presence of TiO$_2$ particles. Previously prepared TiO$_2$ dispersion was mixed with tetraethoxysilane (TEOS) at a volume ratio of 40:1. The weight ratio of TiO$_2$ to TEOS was about 1:1 and the molar ratio Si/Ti was about 0.38. The mixture was stirred for 24 h at room temperature, leading to stable, semi-transparent dispersion of SiO$_2$/TiO$_2$ composite particles. The sol–gel reaction mechanism can be described as Scheme 1.
SiO₂/TiO₂ dispersion drop by drop and stirred for one hour by adding dialyzed copolymer latex into TiO₂ dispersion or 18 different composite particles. All composites were prepared MMA = \text{co-organic/organic weight ratio (inorganic particles: poly}(AA-co-MMA) latexes were prepared by emulsion polymerization in a 250-ml single-necked round reaction bottle with a stirrer. Deionized water, surfactant, initiator, and monomers (AA and MMA) were added into reaction bottle. The amount of monomers and the type of surfactants and initiators used were listed in Table 1. The reaction time and temperature for synthesizing all three latexes were 2.5 h and 80 °C, respectively. Three latexes were stable colloid system without precipitation. The latex surface charge polarity was determined by the surfactant used. SDS and CTAC prepared anionic and cationic latexes, respectively. As for soapless latexes, the surface charge polarity would be negative since KPS was used as initiator, which generated negative charges when dissolved in water. Three latexes were dialyzed in deionized water at room temperature for 3 days for the following characterization and preparation of TiO₂/latex and SiO₂/TiO₂/latex composite particles.

### Table 1

<table>
<thead>
<tr>
<th>AA-co-MMA latex recipe</th>
<th>AA</th>
<th>MMA</th>
<th>H₂O</th>
<th>Surfactant</th>
<th>Initiator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soapless latex</td>
<td>1.08 g</td>
<td>3.5 g</td>
<td>80 ml</td>
<td>–</td>
<td>KPS 0.046 g(^{a})</td>
</tr>
<tr>
<td>Anionic latex</td>
<td>2.16 g</td>
<td>7 g</td>
<td>160 ml</td>
<td>SDS 0.74 g</td>
<td>KPS 0.458 g(^{b})</td>
</tr>
<tr>
<td>Cationic latex</td>
<td>1.08 g</td>
<td>3.5 g</td>
<td>160 ml</td>
<td>CTAC 0.7 g</td>
<td>AIBA 0.09 g(^{c})</td>
</tr>
</tbody>
</table>

\(^{a}\) 1 wt% of monomer.
\(^{b}\) 5 wt% of monomer.
\(^{c}\) 2 wt% of monomer.

#### 2.4. Preparation of poly(AA-co-MMA) latex

Soapless, anionic, and cationic poly(AA-co-MMA) latexes were prepared by emulsion polymerization in a 250-ml single-necked round reaction bottle with a stirrer. Deionized water, surfactant, initiator, and monomers (AA and MMA) were added into reaction bottle. The amount of monomers and the type of surfactants and initiators used were listed in Table 1. The reaction time and temperature for synthesizing all three latexes were 2.5 h and 80 °C, respectively. Three latexes were stable colloid system without precipitation. The latex surface charge polarity was determined by the surfactant used. SDS and CTAC prepared anionic and cationic latexes, respectively. As for soapless latexes, the surface charge polarity would be negative since KPS was used as initiator, which generated negative charges when dissolved in water. Three latexes were dialyzed in deionized water at room temperature for 3 days for the following characterization and preparation of TiO₂/latex and SiO₂/TiO₂/latex composite particles.

#### 2.5. Preparation of TiO₂/latex and SiO₂/TiO₂/latex composite particles

Each of the three different copolymer latexes was mixed with TiO₂ dispersion or SiO₂/TiO₂ dispersion at various inorganic/organic weight ratio (inorganic particles: poly(AA-co-MMA) = 50:50, 70:30, and 80:20, respectively), thus creating 18 different composite particles. All composites were prepared by adding dialyzed copolymer latex into TiO₂ dispersion or SiO₂/TiO₂ dispersion drop by drop and stirred for one hour at room temperature. It could be seen that when copolymer latex was added to TiO₂ dispersion or SiO₂/TiO₂ dispersion, inorganic and organic components combined to form precipitates very quickly. The precipitates were washed by water and then separated from the dispersion supernatant by centrifugation at 8000 rpm for 10 min repeatedly in order to remove the free nanoparticles and dried in vacuum oven. The sample nomenclature rules are: “T” and “ST” represent TiO₂ and SiO₂/TiO₂, and “P,” “AP,” and “CP” represent soapless, anionic, and cationic polymer latex, respectively. For example, T50P50 means composite particles which consist of 50 wt% TiO₂ and 50 wt% soapless latex, ST70CP30 means composite particles which consist of 70 wt% SiO₂/TiO₂ and 30 wt% cationic latex, and so forth.

#### 2.6. Composite particles blending with PET

Composite particles blending with PET was prepared by using blender. The blending procedure was described as following: PET powder was blended with six different composites, respectively (T50P50, T50AP50, T50CP50, ST50P50, ST50AP50, and ST50CP50). The composite amount added was controlled that the content of inorganic component (TiO₂ of SiO₂/TiO₂) was maintained at 1 wt% of PET. The blending process started at room temperature, heating to 90 °C and mixing for 20 min to vaporize the residual water, followed by heating to 270 °C and blending for another 15 min. After finishing the process, the viscous liquid-like product was quickly cooled down to room temperature, which turned to brown or gray solid.

#### 2.7. Characterization

##### 2.7.1. Particle size from dynamic light scattering measurement (DLS) and zeta potential analysis

Particle sizes by DLS and zeta potentials of TiO₂, SiO₂/TiO₂, and three poly(AA-co-MMA) latexes after dialysis were analyzed using a Malvern 4700 Light Scattering Particle Size Analyzer.

##### 2.7.2. X-ray diffraction (XRD) analysis

XRD patterns were taken to analyze TiO₂ and SiO₂/TiO₂ crystal structures, using a MAC Science Diffractometer, with Cu Kα radiation at 40 kV and 30 mA.

##### 2.7.3. Fourier transform infrared spectroscopy (FT-IR) analysis

SiO₂/TiO₂ composite particles were pressed into KBr pellet and the FT-IR spectrum was obtained with BIO-RAD FTS40 in the 4000–400 cm⁻¹ range with 16 scans.

##### 2.7.4. X-ray photoelectron spectroscopy (XPS)

XPS analysis of TiO₂ and SiO₂/TiO₂ particles was performed with a VG MICROTECH MT-500 system and Al Kα (1486.6 eV) as X-ray source. The pressure in the analysis chamber was kept under 10⁻⁷ bar. Spectrum of various samples were fitted and analyzed by considering the integrated peak area of O 1s with SYSTAT PeakFit version 4.11 software.

##### 2.7.5. Acid–base titration experiments

Three copolymer latexes were titrated with 0.1 N NaOH solution to determine the number of COOH group (N_COOH) per gram of copolymer. The pH value was monitored with SUNTEX SP-701 pH/temp/mV meter.

##### 2.7.6. Thermogravimetric analysis (TGA)

TGA analysis, from Perkin-Elmer, with a heating rate of 20 °C/min from room temperature to 800 °C under air atmosphere, was used to estimate the content of inorganic nanoparticles in the composite materials.

##### 2.7.7. Morphology observation

In order to observe the morphology of TiO₂/latex composite and SiO₂/TiO₂/latex composite, composite films were pre-
pared by spin-coating the precipitate part of composite dispersion on glass. The organic component of TiO$_2$/latex and SiO$_2$/TiO$_2$/latex films was quickly burned out at 500 °C for 15 min. Then the distribution of organic and inorganic parts could be recognized by using a Hitachi S-800 scanning electron microscopy (SEM). In addition, morphology observation was also conducted on blended samples of composites with PET by using the same instrument of SEM.

2.7.8. Differential scanning calorimetry (DSC) analysis
For blended samples of composites with PET, the effect of TiO$_2$/latex composites or SiO$_2$/TiO$_2$/latex composites on the thermal and crystallization properties of PET was analyzed, respectively, by DSC with a Perkin-Elmer TA 2010. The experimental method could be described in two parts:

2.7.8.1. Thermal analysis from molten state
Blended samples were heated at a rate of 80 °C/min from room temperature to 290 °C, holding for 5 min to destroy the crystal structure and thermal history of the samples, then cooled at a rate of 10 °C/min to 30 °C to obtain the temperature of crystallization ($T_c$), and reheated at a rate of 10 °C/min to 290 °C to obtain the melting temperature ($T_m$).

2.7.8.2. Thermal analysis from glassy state
Blended samples were heated at a rate of 80 °C/min from room temperature to 290 °C, holding for 5 min, quickly quenching with liquid nitrogen, and then reheated at a rate of 10 °C/min from 30 to 270 °C to obtain the temperatures of glass transition ($T_g$), crystallization ($T'_c$), and melting ($T'_m$).

3. Results and discussion

3.1. Characterization of TiO$_2$, SiO$_2$/TiO$_2$ and poly(AA-co-MMA) latex

3.1.1. Particle size
Generally, a sol–gel reaction of metal alkoxide to form metal oxide could be catalyzed either by acid or by base, leading to different structures of product. In the reaction of preparing TiO$_2$/latex dispersion, nitric acid was added not only as a catalyst but also as a peptizer, which converted the white solid particles into colloidal system during the heating process. The pH of TiO$_2$ dispersion as prepared was 0.67. After reaction with TEOS, the pH was increased to about 1. DLS results showed that the average particle sizes of TiO$_2$ and SiO$_2$/TiO$_2$ were 12.4 and 19.8 nm, respectively, as shown in Table 2. The particle size distributions of both TiO$_2$ and SiO$_2$/TiO$_2$ were also quite narrow, shown in Fig. 1. Latex particle sizes of soapless, anionic, and cationic latexes, also shown in Table 2, were 180, 32.7, and 20 nm, respectively. The particle sizes of latexes were larger than that of TiO$_2$ or SiO$_2$/TiO$_2$, and this size difference would contribute to the interaction between the organic latex and inorganic nanoparticles.

3.1.2. Characterization of TiO$_2$ and SiO$_2$/TiO$_2$
X-ray diffraction patterns of the TiO$_2$ and SiO$_2$/TiO$_2$ powder dried from TiO$_2$ and SiO$_2$/TiO$_2$ dispersions, respectively, were shown in Fig. 2. TiO$_2$ particles possessed peaks at $2\theta = 25.8^\circ$, 38.2°, 47.7°, 55.4°, 63.6°, corresponding to anatase crystalline form [18–20]. After reaction with TEOS, these peaks still remained, though decreasing in intensity, which meant that SiO$_2$ did not affect the crystalline structure of TiO$_2$ significantly.

Table 2
Characterization of TiO$_2$, SiO$_2$/TiO$_2$ and three poly(AA-co-MMA) latex

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size (nm)</th>
<th>Zeta potential (mV)</th>
<th>pH</th>
<th>$N_{COOH}$ a (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>12.4</td>
<td>53.6</td>
<td>0.67</td>
<td>–</td>
</tr>
<tr>
<td>SiO$_2$/TiO$_2$</td>
<td>19.8</td>
<td>33.7</td>
<td>1</td>
<td>–</td>
</tr>
<tr>
<td>Soapless latex</td>
<td>180</td>
<td>−33.9</td>
<td>2.13</td>
<td>3.184</td>
</tr>
<tr>
<td>Anionic latex</td>
<td>32.7</td>
<td>−31.1</td>
<td>2.23</td>
<td>3.304</td>
</tr>
<tr>
<td>Cationic latex</td>
<td>20</td>
<td>19.9</td>
<td>2.20</td>
<td>3.088</td>
</tr>
</tbody>
</table>

a Number of COOH group per gram of copolymer. ($pK_a$ of PAA = 4.25 [25].)
Fig. 3. FT-IR spectrum of SiO₂/TiO₂ particles.

A large peak around $2\theta = 20^\circ$ might be contributed by the presence of SiO₂. By comparing the size of TiO₂ and SiO₂/TiO₂ particles as mentioned in Fig. 1, it can be deducted that SiO₂ incorporated with TiO₂ particles to form larger SiO₂/TiO₂ composite particles.

The incorporation of Si and Ti could be evidenced from the following points:

1. From the sol–gel reaction mechanism of TEOS in the presence of TiO₂ particles, as shown in Scheme 1, Si–O–Si bonds formed through Eqs. (2) and (3), and Si–O–Ti bonds formed through Eq. (4). That means SiO₂/TiO₂ composite particles formed from this sol–gel reaction.
2. From DLS measurement in Fig. 1, sizes of TiO₂ and SiO₂/TiO₂ particles measured were 12.4 and 19.8 nm, respectively. Both dispersions showed one-peak size distribution curves, indicating TEOS effectively reacted onto TiO₂ particles.
3. From FT-IR analysis of SiO₂/TiO₂ in Fig. 3, a small peak appeared at 940–960 cm$^{-1}$, which was attributed to Ti–O–Si bonds [21].
4. From XPS analysis of SiO₂/TiO₂ particles in Fig. 4, the peak at 530 eV was assigned as O 1s of Ti–O–Ti, and 532 eV as O 1s of Si–O–Si [22].

Then from the O 1s spectrum of SiO₂/TiO₂ composite particles, the Si–O–Si/Ti–O–Ti mole ratio was calculated to be 1.8. Since molar ratio of Si/Ti was 0.38 in feed, much smaller than the ratio of 1.8 from XPS measurement, this indicated that a large portion of surface of TiO₂ particles was covered by SiO₂ particles. This also proved that SiO₂ particles were located at the surface of TiO₂ particles.

3.1.3. Zeta potential of TiO₂, SiO₂/TiO₂ and poly(AA-co-MMA) latexes

Zeta potentials of TiO₂ and SiO₂/TiO₂, listed in Table 2, were 53.6 and 33.7 mV, respectively, which meant that the inorganic particles were positively charged. Zeta potentials of soapless latex and anionic latex were −33.9 and −31.1 mV, respectively. The pH values of latexes and pKₐ of AA were also listed in Table 2. The pH values of latexes were smaller than pKₐ of AA. Therefore, for soapless polymer latex, negative charges were resulted from negative initiator KPS. For anionic polymer latex, negative charges were contributed not only from initiator but mostly from negative charged surfactant SDS. Heterocoagulation took place when inorganic dispersion (TiO₂ or SiO₂/TiO₂) mixed with polymer latex. The interaction between inorganic particles and soapless latex or anionic latex particles was mainly resulted from the electrostatic force of opposite charge attraction. On the other hand, zeta potential of cationic latex was 19.9 mV. For cationic latex, positive charges were resulted from positive initiator AIBA and positive charged surfactant CTAC. It was expected that inorganic particles and cationic latex should form stable suspension system by electrostatic charge repulsion. However, precipitation appeared immediately after cationic latex was added to TiO₂. Heterocoagulation occurred during the mixing process. It was presumably due to the following reasons:

1. pH-induced latex coagulation: The pH of cationic latex was about 2.20, higher than that of TiO₂ dispersion. The low pH of TiO₂ dispersion destroyed the stability of cationic latex, causing latex particles to coagulate and precipitate along with TiO₂ nanoparticles.
2. The hairy AA block segments located at outer surface of poly(AA-co-MMA) latex particles for it is highly hydrophilic [23]. Therefore TiO₂ still possibly interacted with cationic latex through carbonyl group–titanium chelation [24] or hydrogen bonding, even though positive charge repulsion existed between these two components.

An acid–base titration experiment was conducted to estimate the COOH groups on latex particles as shown in Table 2. From acid–base titration experiments the pH and the number of COOH group per gram of copolymers was very close for three latexes, which indicated that most of the AA segments located on the surface of latex particles.
3.2. TGA analysis of TiO$_2$/latex composite and SiO$_2$/TiO$_2$/latex composite

3.2.1. TGA of TiO$_2$/latex composites

TGA experiment of the precipitated composites could give direct evidence about the formation of nanocomposites by heterocoagulation. From the TGA experiments, almost no residual was left after 500 °C for pure polymer latex while TiO$_2$ remained high weight percentage at 800 °C (87.6%). TGA residual weight percentages at 800 °C of TiO$_2$/soapless latex composite, TiO$_2$/anionic latex composite and TiO$_2$/cationic latex composite, shown in Table 3, fell between the values of pure polymer and TiO$_2$. It indicated the fact of TiO$_2$ nanocomposites formed by heterocoagulation. TGA of poly(AA-co-MMA) indicated a two-step degradation around 200–300 °C and 300–400 °C, referred to AA and MMA degradation, respectively. Though composition of residual was complicated since it might consist of TiO$_2$ particles, TiO$_2$ precursors with representative carbon content, and other carbon compounds bonded to TiO$_2$ surface, it gave information of the adsorbed amount of inorganic nanoparticles on polymer particles. It was observed that the color of TGA residuals at 800 °C of TiO$_2$/soapless and TiO$_2$/anionic latex composites was black, implying strong interaction between TiO$_2$ and latex particles, whereas grey or grey-white residual presented with TiO$_2$/cationic latex composites, indicating a weaker interaction between TiO$_2$ and cationic latex particles. Also from Table 3, the TGA results of three TiO$_2$/latex composites exhibited the same trend that the higher the content of TiO$_2$, the higher the residual weight percentage. The interaction of inorganic and negative charged latex particles was mainly dominated by electrostatic force. Therefore the residual weight of TiO$_2$/anionic latex composite was higher than that of TiO$_2$/cationic latex composite. The low residual weight percentage of TiO$_2$/soapless latex composites could be explained by the decrease of total surface area of polymer latex particles. From Table 2 it is known that the size of soapless latex particles was about 5–6 times larger than anionic latex particles. Consequently, the total surface area of soapless latex particles was much smaller and the effective adsorption of TiO$_2$ particles largely decreased.

The degradation temperature at 5 wt% loss ($T_d$) from TGA curves were also listed in Table 3. Fig. 5 shows the TGA curves of TiO$_2$/anionic latex composites. Generally, the variation of onset temperature was contributed by the existence of small molecular weight species. In our system, $T_d$ of nanocomposite was mainly affected by (1) TiO$_2$ precursors with representative carbon content, and other organic compounds bonded to TiO$_2$ surface, and (2) surfactants of polymer latexes. The interaction of these species would be complicated since the contents of inorganic nanoparticles and organic polymer latexes varied in the experiments. A general trend could be observed for our system that the range of $T_d$ of each system decreased as the residual weight percentage of the nanocomposite increased. In other words, $T_d$ decreased when the content of TiO$_2$ increased in the nanocomposite. The effect resulted from inorganic particles on $T_d$ was more significant than that resulted from surfactants of polymer latexes.

3.2.2. TGA of SiO$_2$/TiO$_2$/latex composites

When SiO$_2$/TiO$_2$ was used instead of TiO$_2$, the positive charge density on the surfaces of inorganic particles decreased since the zeta potential lowered, shown in Table 2. However the attraction between SiO$_2$/TiO$_2$ and negative charged latex remained strong. Table 3 shows the TGA residual weight percentage of SiO$_2$/TiO$_2$/latex composites at 800 °C. The size and weight of each SiO$_2$/TiO$_2$ particles were larger than TiO$_2$, causing the residual weight percentage of SiO$_2$/TiO$_2$/latex composites to be higher than that of TiO$_2$/latex composites. It was observed that higher SiO$_2$/TiO$_2$ content resulted in higher

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
 & \textbf{$T_d$ (°C)} & \textbf{Residual wt\%} \\
\hline
\hline
TiO$_2$/soapless latex & & \\
T50P50 & 205.0 & 40.8 \\
T70P30 & 204.6 & 41.5 \\
T80P20 & 180.9 & 52.2 \\
\hline
TiO$_2$/anionic latex & & \\
T50AP50 & 181.6 & 46.2 \\
T70AP30 & 171.6 & 57.9 \\
T80AP20 & 155.8 & 60.6 \\
\hline
TiO$_2$/cationic latex & & \\
T50CP50 & 164.2 & 40.0 \\
T70CP30 & 148.5 & 48.1 \\
T80CP20 & 141.2 & 55.1 \\
\hline
SiO$_2$/TiO$_2$/soapless latex & & \\
ST50P50 & 162.5 & 76.68 \\
ST70P30 & 148.5 & 71.23 \\
ST80P20 & 146.0 & 72.00 \\
\hline
SiO$_2$/TiO$_2$/anionic latex & & \\
ST50AP50 & 197.1 & 55.9 \\
ST70AP30 & 188.6 & 68.7 \\
ST80AP20 & 167.2 & 72.4 \\
\hline
SiO$_2$/TiO$_2$/cationic latex & & \\
ST50CP50 & 204.0 & 38.7 \\
ST70CP30 & 193.0 & 59.8 \\
ST80CP20 & 170.3 & 64.8 \\
\hline
\end{tabular}
\caption{Degradation temperatures at 5 wt% loss ($T_d$) and residual weight percentage from TGA curves.}
\end{table}
adsorption amount on latex polymer particles, and negative charged latex polymer particles presented stronger interaction with SiO\(_2\)/TiO\(_2\) particles. The residual weight was unexpectedly high for SiO\(_2\)/TiO\(_2\)/soapless latex composite. It might be due to size difference between latex particles and SiO\(_2\)/TiO\(_2\) particles, leading to more compact arrangement of particle adsorption. Therefore, in the case of SiO\(_2\)/TiO\(_2\) particles, higher adsorption amount could be achieved by using larger latex polymer particles.

Similar to the results of TiO\(_2\)/polymer composites, \(T_d\) of SiO\(_2\)/TiO\(_2\)/polymer composites also decreased as residual weight percentage increased, as shown in Table 3. Precursors with representative carbon content and other organic compounds bonded to inorganic surface were contributed not only from TiO\(_2\) but also SiO\(_2\) in this system. Again this result indicated that the effect resulted from inorganic particles on \(T_d\) was more significant than that resulted from surfactants of polymer latexes.

### 3.3. Morphology of TiO\(_2\)/latex composite and SiO\(_2\)/TiO\(_2\)/latex composite

#### 3.3.1. Morphology of TiO\(_2\)/latex composite

SEM of the burned precipitated TiO\(_2\)/soapless latex composite, TiO\(_2\)/anionic latex composite and TiO\(_2\)/cationic latex composite were shown in Fig. 6. Through burning the TiO\(_2\)/latex composite at 500 °C to remove the polymer component, we could observe the distribution of inorganic and organic component of TiO\(_2\)/latex composite from the residual morphology. The dark regions and white regions represented the polymer and TiO\(_2\), respectively. Here it was assumed that after burning at 500 °C, almost no organic components were present and only inorganic components were left. In the SEM of TiO\(_2\)/cationic latex composite (T50CP50, Fig. 6c), white small particles, regarded as TiO\(_2\) particles, showed homogeneous distribution, with no obvious aggregation. On the other hand, in Fig. 6a, large aggregations of TiO\(_2\) particles, with region of 200–300 nm which was about the size of soapless latex particles (Fig. 6d) were apparent in the SEM of TiO\(_2\)/soapless latex composite, whereas the morphology of TiO\(_2\)/anionic latex composite showed less aggregation than TiO\(_2\)/soapless latex composite. These morphology observations indicated that stronger interaction existed between particles through electrostatic force.

#### 3.3.2. Morphology of SiO\(_2\)/TiO\(_2\)/latex composite

SEM of the burned SiO\(_2\)/TiO\(_2\)/soapless latex composite, SiO\(_2\)/TiO\(_2\)/anionic latex composite and SiO\(_2\)/TiO\(_2\)/cationic latex composite were shown in Fig. 7. Compared with the corresponding TiO\(_2\)/soapless latex composites, morphology of burned SiO\(_2\)/TiO\(_2\)/soapless latex composites was more homogeneous, with aggregation region of 60–100 nm. As for SiO\(_2\)/TiO\(_2\)/anionic latex composite and SiO\(_2\)/TiO\(_2\)/cationic latex composites, the residual components of both these two samples were homogeneously distributed SiO\(_2\)/TiO\(_2\) particles. These results suggested that when SiO\(_2\)/TiO\(_2\) was used, aggregation of inorganic particles was less apparent, therefore these inorganic particles could be homogeneously distributed in SiO\(_2\)/TiO\(_2\)/latex composites in comparison with TiO\(_2\)/latex composites.

### 3.4. Morphology of PET blended with SiO\(_2\)/TiO\(_2\)/latex composite

The SEM observations of PET blended with three SiO\(_2\)/TiO\(_2\)/latex composites were shown in Fig. 8. Each blended sample was fractured in liquid nitrogen for observing both the surface and fractured faces. In PET blended with SiO\(_2\)/TiO\(_2\)/cationic latex, almost no local aggregation existed, whether in surface or fractured face, which meant that cationic composites were well incorporated with PET. It was believed that this incorporation can be explained by a favorable interaction between the chains of the acrylic copolymer nanoparticles, CTAC positive motifs and the functional groups of PET. On the contrary, when PET was blended with SiO\(_2\)/TiO\(_2\)/soapless latex or SiO\(_2\)/TiO\(_2\)/anionic latex, it was easy to find small regions of aggregation, even that the content of inorganic part of each composite was only 1 wt% of PET. These aggregations were believed to be composites unable to blend with PET, resulting probably from the repulsion of negative charged composite particles and the electron–rich carbonyl functional groups on the main chain of PET. Therefore it could be concluded that the cationic composites associated with PET better than the anionic composites. The morphology observation results of PET blended with TiO\(_2\)/latex composite were quite similar to those of PET blended with SiO\(_2\)/TiO\(_2\)/latex composites.

#### 3.5. DSC analysis of PET blended with cationic charged composites

##### 3.5.1. \(T_c\), \(\Delta H_c\), and \(T_m\) (DSC analysis from the molten state)

From the above morphology observation of PET blended with different TiO\(_2\)/latex or SiO\(_2\)/TiO\(_2\)/latex composites, it was known that cationic composites incorporated with PET better than anionic composites did. Therefore we evaluated only the effect of cationic composites on the thermal and crystallization properties of PET, including the heat and the temperature of crystallization, glass transition, and melting, by differential scanning calorimetry (DSC). The cooling and the subsequent reheating curves were shown in Figs. 9 and 10, to read the temperature of crystallization \(T_c\), melting temperature \(T_m\), and heat of crystallization \(\Delta H_c\), respectively. The data of \(T_c\), \(\Delta H_c\), and \(T_m\) are listed in Table 4. Table 4 shows that the temperatures of crystallization (\(T_c\)) of PET blended with cationic composites, T50P50 and ST50CP50, were lowered by 7 and 9 °C, respectively, compared with pure PET, which has \(T_c\) of 214.22 °C. The decrease in \(T_c\) implied that the presence of cationic composites affected the mobility and packing of PET molecular chains, resulting in crystallization occurred at lower temperature. The melting peak of PET in DSC usually appeared at 244.8 °C with a smaller shoulder at higher temperature around 249 °C. However, in Fig. 11, the higher temperature shoulder was largely amplified and became a major peak after PET blended with the cationic composites. One possible reason was that the PET molecules blended with TiO\(_2\)/cationic
latexes or SiO₂/TiO₂/cationic latexes crystallized slower in the cooling process, resulting in higher order of crystalline packing, thus the higher melting temperature peak was significantly enhanced. To sum up, the molecular arrangement and crystallization of PET was deterred after PET blended with the composites.

3.5.2. \( T_g, T'_c, \Delta H'_c, T'_m \) (DSC analysis from glassy state)

Fig. 11 shows the heating curves of PET blended with cationic composites from the glassy state. \( T_g \)'s of blended PET were increased by 3 °C from 73.9 °C of pure PET. Temperature of crystallization \( (T'_c) \) of blended PET was also increased compared to pure PET. As for the effect of cationic composites on the melting temperature \( (T'_m) \) of blended PET, the \( T_m \)'s were slightly higher compared to 250.2 °C of pure PET. Considering together with the results mentioned in previous section, the temperature range of crystallization \( (T_c-T'_c) \) of PET blended with cationic composites was narrowed compared with pure PET, whereas degree of crystallization remain almost the same since
the heat of crystallization did not change significantly. It could be sure that cationic composites hinder the molecular motion of PET to some extent. Therefore $T_g$’s were increased, melting temperatures ($T_m$ or $T'_m$) were increased, and temperature range of crystallization was narrowed.

Considering the increase of $T_g$ of PET in the blend, two factors caused this result: (1) the incorporation of poly(AA-co-MMA) copolymers and (2) the rigid component of inorganic particles. In our experiments of blending, the weight ratio of copolymer to PET was less than 1%. $T_g$’s of PET and poly(AA-co-MMA) were around 73.9°C and 110°C, respectively. If the effect of poly(AA-co-MMA) on $T_g$ of PET was predicted by Fox’s equation, the $T_g$ of PET was at most increased by 0.5°C. But DSC data showed that $T_g$ of PET was increased by 3°C after blending. Therefore the inorganic particles play more important role on the hindrance of chain motion of PET.

Finally, PET was blended with pure TiO$_2$ or SiO$_2$/TiO$_2$ particles. Similar effect on the PET thermal properties could also be observed shown in Table 4. It was worth to mention that $\Delta H_c$ value increased more significantly for systems...
of PET/SiO$_2$/TiO$_2$ and PET/TiO$_2$. It implied that TiO$_2$ or SiO$_2$/TiO$_2$ particles played the role of nucleation agent in the blend particularly when crystallization temperature was high.

4. Conclusions

In this paper synthesis of TiO$_2$/latex and SiO$_2$/TiO$_2$/latex composites by using the concept of heterocoagulation were performed. Nano-sized TiO$_2$ dispersions with anatase crystalline form were prepared by acid catalyzed sol–gel reaction in water. TEOS reacted with TiO$_2$ dispersion to form SiO$_2$/TiO$_2$ nanoparticles through formation of Si–O–Ti bond and the particle size was increased while the crystalline form of TiO$_2$ was not altered. Poly(AA-co-MMA) latexes were synthesized by using different initiators and surfactants in the process of polymerization. By mixing TiO$_2$ dispersion with different poly(AA-co-MMA) latexes, negative charged soapless latex and anionic latex showed stronger interaction with TiO$_2$ particles than cationic latex, which was supported by the TGA results. The soapless latex polymer particles showed lower ability of adsorption to TiO$_2$ particles, due to the decrease of total surface area of these larger particles. If SiO$_2$/TiO$_2$ particles were used in-

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Fig. 8. SEM of PET blended with (a) ST50P50, (b) ST50AP50, and (c) ST50CP50.
Fig. 9. DSC analysis from molten state: cooling curve of PET blended with (a) T50CP50 and (b) ST50CP50.

Fig. 10. DSC analysis from molten state: reheating curve after (a) T50CP50 and (b) ST50CP50.

Fig. 11. DSC analysis from glassy state of PET blended with (a) T50CP50 and (b) ST50CP50.

Table 4

<table>
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<tr>
<th>Sample</th>
<th>$T_c$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$T_g$ (°C)</th>
<th>$T_c'$ (°C)</th>
<th>$T_m'$ (°C)</th>
<th>$\Delta H_c'$ (J/g)</th>
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<td>PET</td>
<td>214.22</td>
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<td>77.57</td>
<td>123.59</td>
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<tr>
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<td>248.91</td>
<td>44.11</td>
<td>77.17</td>
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<td>251.46</td>
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stead of TiO$_2$ particles, unexpected high adsorption result was observed. The TGA degradation curves of both TiO$_2$/latex and SiO$_2$/TiO$_2$/latex composites showed the same general trend that $T_d$ of each system decreased as the residual weight percentage of the nanocomposite increased. The stronger interaction between TiO$_2$ and negative charged latexes was also supported by SEM observation since morphologies of burned TiO$_2$/soapless latex and TiO$_2$/anionic latex composites were less homogeneous.

When blending with PET, TiO$_2$/cationic latex and SiO$_2$/TiO$_2$/cationic latex exhibited better incorporation with PET because more homogeneous morphology was observed. Therefore the presence of TiO$_2$/latex or SiO$_2$/TiO$_2$/latex composites affected the thermal and crystallization properties of PET. From DSC result, $T_g$ and $T_m$ of PET were increased while the temperature range of crystallization was narrowed. Similar effects were also observed when PET was blended with only pure TiO$_2$ and SiO$_2$/TiO$_2$ particles.

Acknowledgment

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References