SYNTHESIS OF CORE-SHELL TIO$_2$/POLYSTYRENE NANOCOMPOSITE BY A CONTINUOUS SPRAY OF LIQUID SOLUTION INTO COMPRESSED CO$_2$

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TiO$_2$/polystyrene (PS) nanocomposite particles without coalescence were generated by precipitation with a compressed fluid antisolvent (PCA) technique in which a toluene solution containing PS and the dispersed TiO$_2$ particles was sprayed into a compressed CO$_2$ environment. The antisolvent CO$_2$ continuously passed through a precipitator with an inner diameter of 5 cm and a total volume of 600 mL, equipped with a hollow cone nozzle with a diameter of 0.41 mm. TiO$_2$ particles with an average size of 21 nm were dispersed well in toluene using the dispersant Disperbyk-180 with the aid of ultrasound. A satisfactory dispersion was essential to yield TiO$_2$/PS nanocomposite particles without coalescence. The SEM images show that nano-sized TiO$_2$/PS particles could only be generated under the conditions that both vapor and liquid CO$_2$ were present and the liquid CO$_2$ level was at one-fourth of the precipitator. From the TEM images, the TiO$_2$/PS core-shell nanocomposite particles without coalescence were found to be generated at a PS concentration of 0.72 wt% and a PS/TiO$_2$ weight ratio of 8.

INTRODUCTION

The methods using supercritical or compressed fluids to generate micro or nano particles can be classified into two categories: rapid expansion of supercritical solution (RESS) and precipitation with a compressed fluid antisolvent (PCA). The applications of RESS are generally limited to the low solubility of polymeric materials in supercritical fluid [1] and to the operation at high pressures. In a PCA process, the dissolution of antisolvent expands the solvent and causes precipitation of the solutes from solvent.
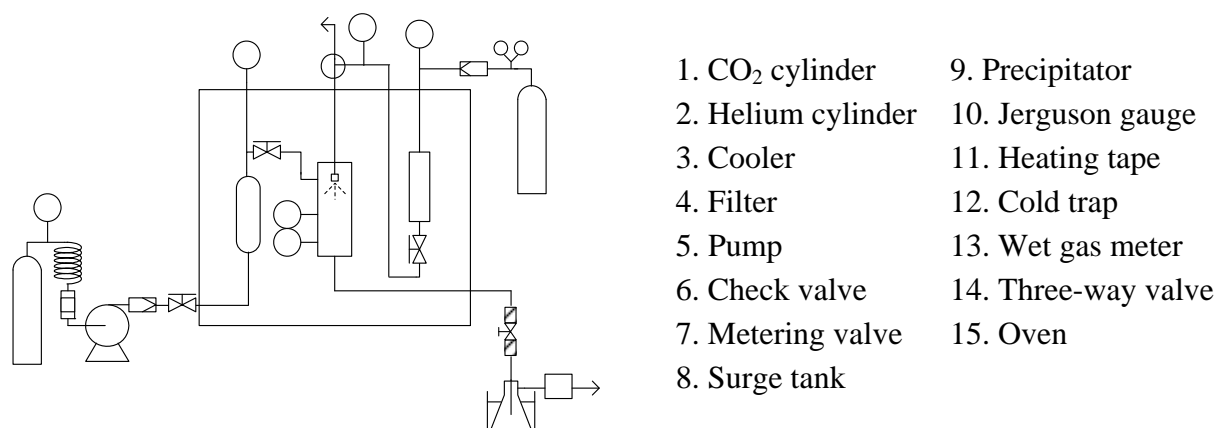
Many particles with different morphology and size have been reported to be generated using PCA techniques [2-15]. This study employs a continuous PCA operation instead of the batch operation reported by Zhang et al. [11]. In a batch PCA operation, CO$_2$ was introduced into a vessel containing the prepared inorganic/polymer dispersion solution and a CO$_2$-expanded solution was therefore formed. When sufficient CO$_2$ was added, a supersaturation of polymer was reached, and a coating started to form on the surfaces of inorganic particles within the CO$_2$-expanded solution. By contrast, in the continuous PCA process used in this study, the prepared dispersion solution was sprayed into a vessel filled with CO$_2$ to form fine droplets via a nozzle, and mass transport started to occur when droplets contacted with CO$_2$. Solvent could be continuously removed by CO$_2$ stream during the process and therefore the accumulation of solvent inside the vessel could also be avoided. Because the possibility of polymer re-dissolved into the solvent decreased, the continuous process yielded a higher production rate of obtained composites than the batch operation.

The objective of this study was to generate TiO$_2$/PS nanocomposite particles in a continuous

PCA operation in which a toluene solution containing PS and the dispersed TiO_2 was sprayed into a compressed CO_2 environment. The operation variables including temperature, pressure, liquid CO_2 level in the precipitator, PS concentration, and PS/TiO_2 weight ratio were varied to examine their effects on the morphology and size of the precipitated TiO_2/PS nanocomposites.

EXPERIMENTAL

The experimental apparatus used for the synthesis of core-shell TiO_2/polystyrene nanocomposites by a continuous spray of liquid solution into compressed CO_2 is illustrated in Figure 1.

1. CO_2 cylinder	9. Precipitator
2. Helium cylinder	10. Jerguson gauge
3. Cooler	11. Heating tape
4. Filter	12. Cold trap
5. Pump	13. Wet gas meter
6. Check valve	14. Three-way valve
7. Metering valve	15. Oven
8. Surge tank	

**Figure 1** : Experimental apparatus

PS (MW 200,000; M_w/M_n 2.23) was purchased from Scientific Polymer Co. TiO_2 nanoparticles (21 nm) were purchased from Degussa (Aeroxide® TiO_2). Toluene (purity 99.97%) was purchased from Echo Chemical, and the dispersant Disperbyk-180 was purchased from BYK-Chemie USA Inc. CO_2 (purity 99.5%) and helium (purity of 99.99%) were purchased from Boclh Industrial Gases. All materials were used as received.

During the continuous PCA operation, the compressed CO_2 passed through the precipitator continuously at a desired temperature and pressure. A 5 g of the solution containing toluene, PS, the dispersed TiO_2 and the dispersant for TiO_2 was first mixed in an ultrasonic bath for 1 h and then the well-agitated solution was loaded into a Jerguson Gauge. The solution was introduced into the precipitator by high pressure helium gas through a nozzle with an inner diameter of 0.41 mm. When the spray process was finished, the compressed CO_2 was allowed to flow through the precipitator continuously for 1 h to remove toluene retained on the precipitated materials. After this extraction process, the pressure inside the precipitator was reduced and the precipitated materials on the filter were collected.

RESULTS AND DISCUSSION

After an extensive study in different ranges of temperature and pressure, submicron-sized TiO_2/PS nanocomposite particles without coalescence could only be generated in the operations in which both CO_2 vapor and liquid coexisted in the precipitator and the liquid level was maintained at a certain level of the precipitator for a CO_2 flow rate of 6000 mL/min and an injected solution flow rate of 130 mL/min. For the operation in which only vapor CO_2 existed in the precipitator (Figure 2b), the solution would be atomized to fine droplets after

spraying into the precipitator via a nozzle. During the path of fine droplets traveled in the vapor CO_2, mutual diffusion occurred simultaneously. CO_2 diffused into droplets and swelled the toluene solution, at the same time toluene also diffused out of droplets and into the CO_2 stream due to the concentration gradient. Therefore, the nucleation of polymer-rich phase within fine droplets began to occur. Because the removing rate of toluene solution within droplets wasn't high enough due to the lower density of vapor CO_2, the former fine droplets adhered together again and a bulky nanocomposite was therefore formed resulting from the growth of PS on the surfaces of TiO_2 nanoparticles.
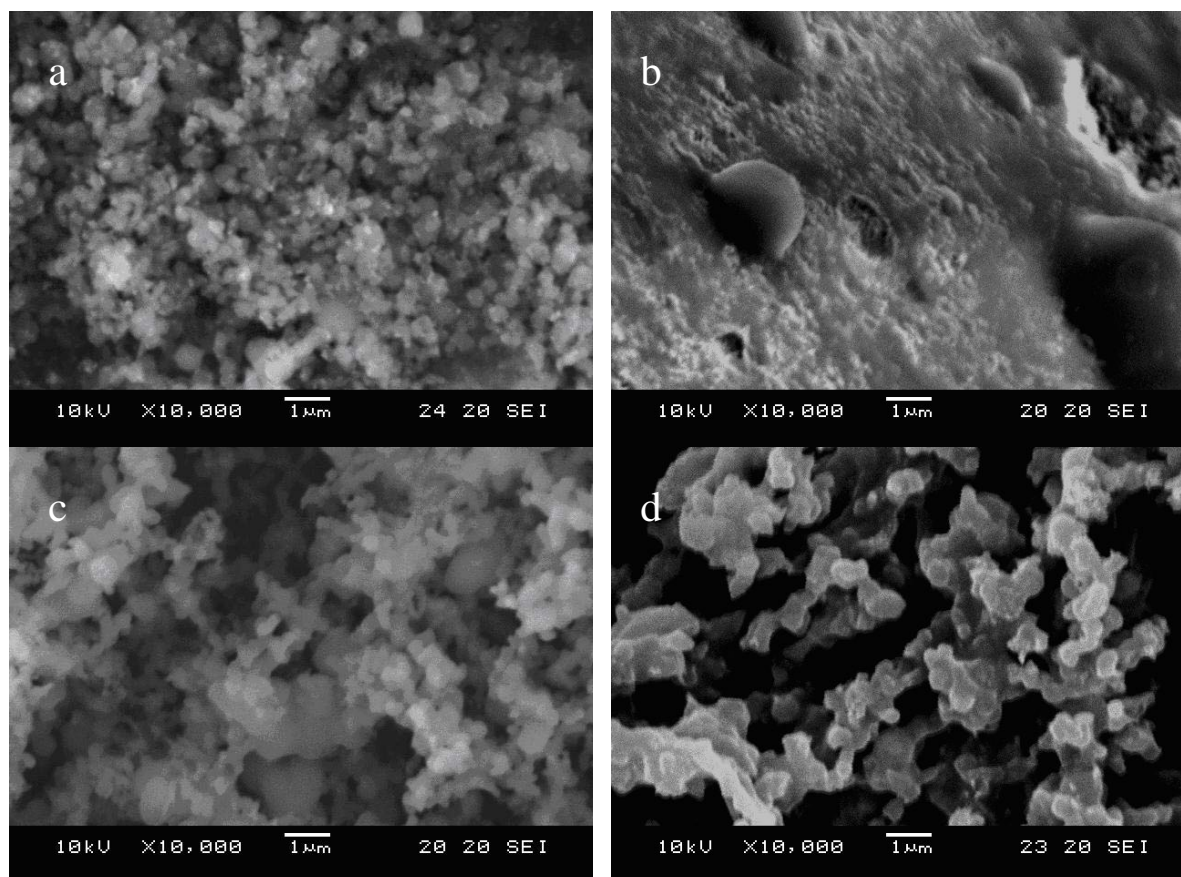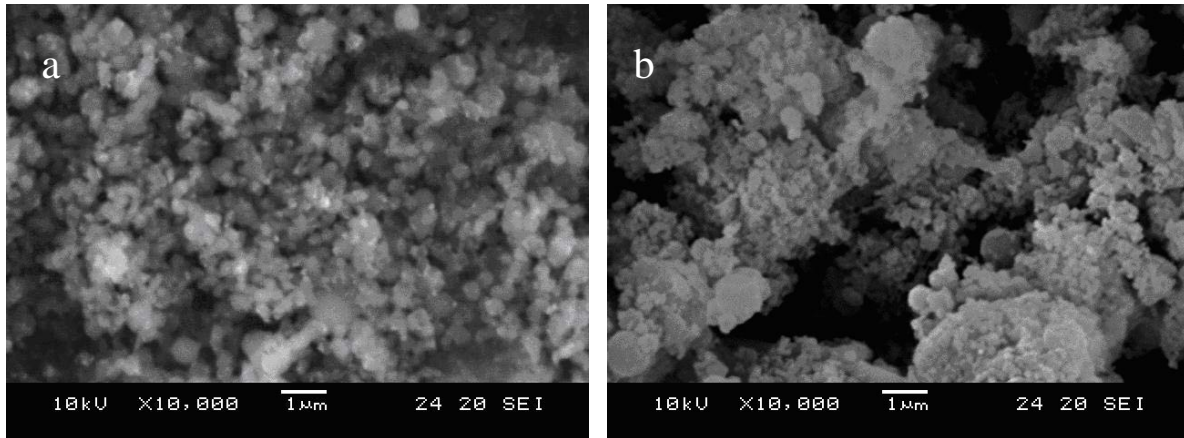

Figure 2 : SEM images of the precipitated nanocomposites at a PS concentration of 0.48 wt%, a dispersant/TiO_2 ratio of 0.6, a PS/TiO_2 ratio of 8 for the temperatures and pressures as (a) 298 K, 6.41 MPa, (b) 298 K, 6.21 MPa, (c) 298 K, 8.28 MPa, and (d) 308 K, 8.28 MPa

When the pressure was increased from 6.21 to 8.28 MPa at which only liquid CO_2 was present in the precipitator, the observed coalescence shown in Figure 2c was believed to result from a relatively poor formation of fine droplets after the solution left the nozzle. The explanation might be applied to the supercritical antisolvent operation (Figure 2d) as well, because similar coalescence occurred. For the trial in which both vapor and liquid CO_2 existed in the precipitator (Figure 2a), fine droplets of the sprayed solution were formed in CO_2 vapor phase and vitrified after falling into the CO_2 liquid phase. For the polymer/toluene systems using CO_2 or HFC-134a as the antisolvent, a nucleation and growth mechanism in which nucleation mainly occurred in vapor phase and growth occurred in liquid phase was suggested [5,9]. When droplets fell into the liquid phase of CO_2, mass transport was speeded

due to the higher density of liquid CO_2. Consequently, the main mechanism during this step was the growth of PS on the surfaces of TiO_2 particles.

In all the runs, over 90% of the injected mass could be collected in the precipitator. Yield is defined as the ratio of the collected mass in the precipitator to the injected mass. Figure 3 illustrates the significant effect of liquid CO_2 level on morphology of the collected nanocomposites. It can be seen that submicron-sized and nearly spherical particles could only be formed for a liquid CO_2 level of 1/4 of the precipitator, and a severe coalescence of the resulting nanocomposites happened at a liquid CO_2 level of 1/2 of the precipitator.
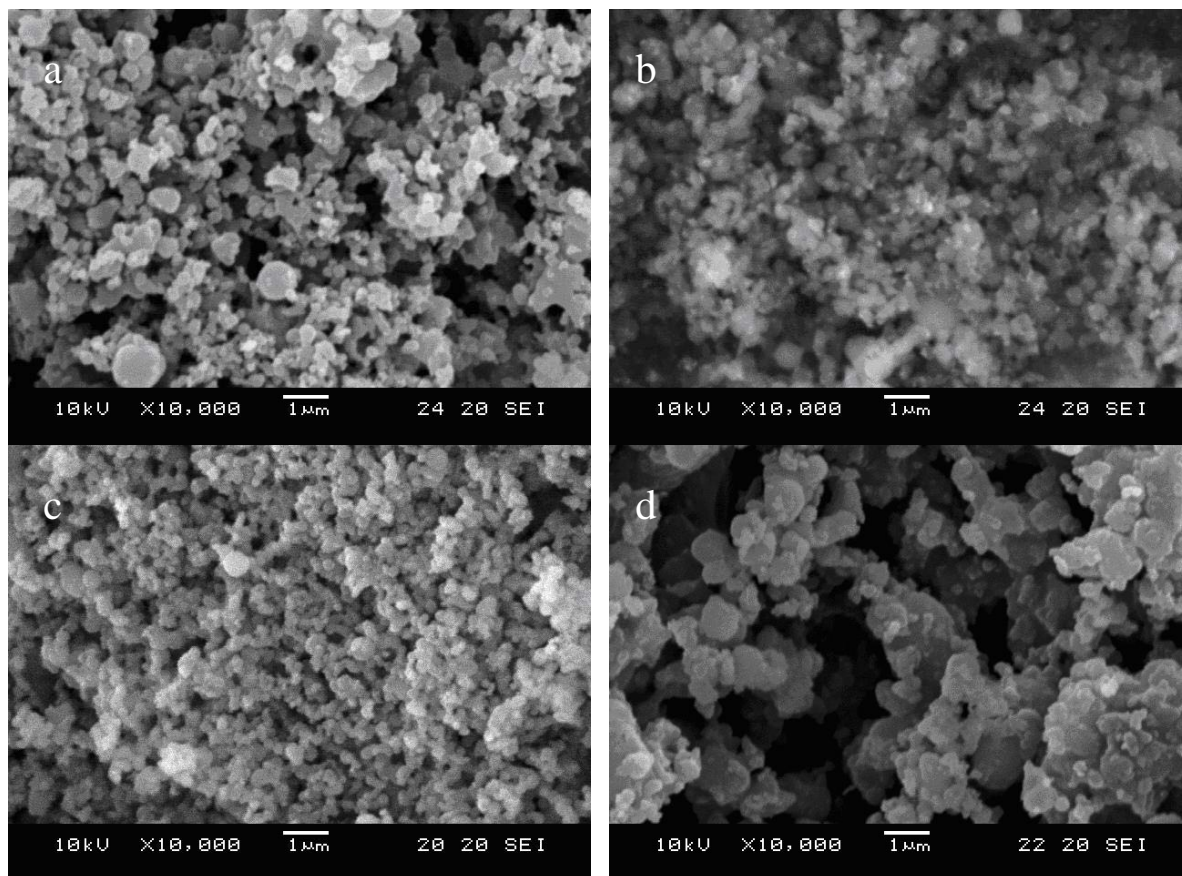

Figure 3 : SEM images of the precipitated nanocomposites at a PS concentration of 0.48 wt%, a PS/TiO_2 ratio of 8, a dispersant/TiO_2 ratio of 0.6, and a liquid CO_2 level of (a) 1/4, (b) 1/2 of the precipitator

For a liquid CO_2 level of 1/4 of the precipitator and a PS concentration in feed of 0.48 wt%, the dependence of the morphology of the collected TiO_2/PS nanocomposites on PS/TiO_2 weight ratio was examined. When the ratio was 2 and 4, TiO_2/PS composite particles with severe coalescence and some TiO_2 particles on the surface of the precipitated composites occurred. This was due to an addition of excess TiO_2 particles in the toluene solution. When the ratio of PS/TiO_2 was at 6 and 8, individual submicron-sized particles could be generated, but a coalescence of nanocomposites occurred when the ratio was increased to 10.

When a liquid CO_2 level of 1/4 of the precipitator and a PS/TiO_2 weight ratio of 8 were fixed in the operation, Figure 4 shows that individual submicron-sized TiO_2/PS nanocomposite particles could only be generated for a PS concentration equal to and lower than 0.72 wt%.

Figure 5 presents the TEM images of the precipitated TiO_2/PS nanocomposite particles. It can be seen that TiO_2 particles were indeed encapsulated in PS matrix, but the core size of the formed nanocomposites was larger than the original size of the TiO_2 nanoparticles, suggesting an aggregation of the dispersed TiO_2 in the operation. The same situation was also reported in Wang et al. [10]. It can also be seen from Figure 5 that nearly spherical TiO_2/PS core-shell nanocomposite particles could be generated at a PS/TiO_2 weight ratio of 8 and a PS concentration of 0.72 wt%.

Figure 4 : SEM images of the precipitated nanocomposites at a PS/TiO$_2$ ratio of 8, a dispersant/TiO$_2$ ratio of 0.6, and a PS concentration of (a) 0.36 wt%, (b) 0.48 wt%, (c) 0.72 wt%, and (d) 1 wt%
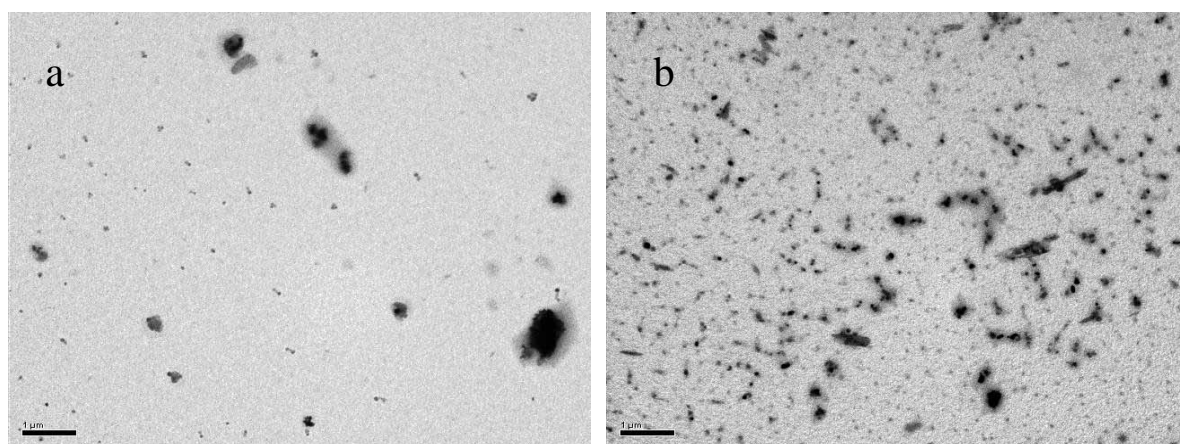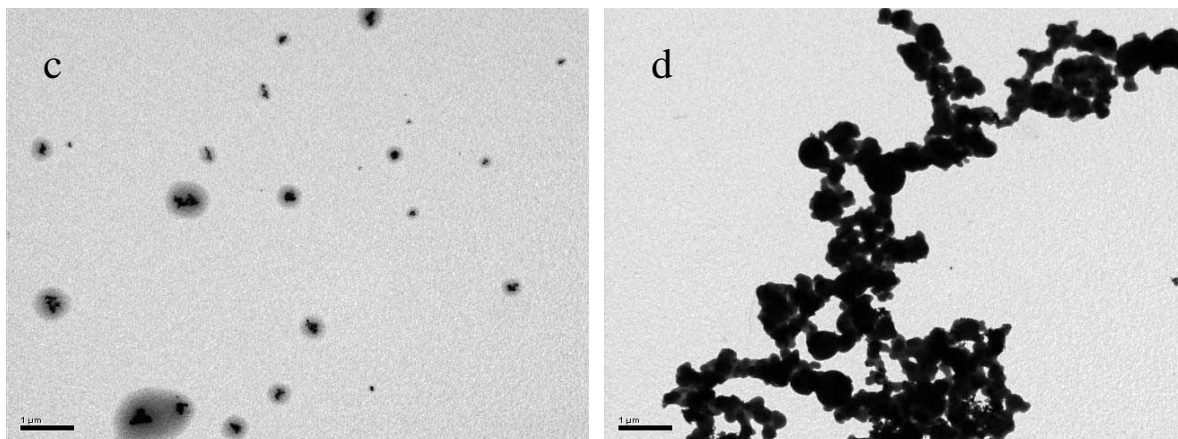
Figure 5 : TEM images of the precipitated nanocomposites at a PS/TiO$_2$ ratio of 8, a dispersant/TiO$_2$ ratio of 0.6, and a PS concentration of (a) 0.36 wt%, (b) 0.48 wt%, (c) 0.72 wt%, and (d) 1 wt%

CONCLUSIONS

The TiO$_2$/PS core-shell nanocomposite particles could be obtained from a continuous antisolvent operation. The precipitator was equipped with a nozzle of 0.41 mm in diameter used for injection and both vapor and liquid CO$_2$ existed in a precipitator with an inner diameter of 5 cm and a total volume of 600 mL. At 298 K and 6.41 MPa, the most appropriate liquid CO$_2$ level was found to be at 1/4 of the precipitator. Nearly spherical TiO$_2$/PS core-shell nanocomposite particles without coalescence could be generated for a PS concentration of 0.72 wt% and a PS/TiO$_2$ weight ratio of 8, indicating that the TiO$_2$ nanoparticles could act as the nuclei in the precipitation.

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