Composite Materials of Thermo-responsive Polymer Networks and Inorganic Nanoparticles

Cecil Coutinho, David Walker, Maya Trotz and Vinay K. Gupta
Department of Chemical Engineering, University of South Florida,
4202 E Fowler Avenue, ENB 118, Tampa, FL 33620

ABSTRACT: The focus of this work is on composite materials of inorganic nanoparticles such as TiO_2 embedded within microspheres of a responsive polymeric network. Microgels of N-isopropylacrylamide (NIPAM) with interpenetrating (IP) linear chains of poly(acrylic acid) (PAAc) were synthesized to promote the incorporation of TiO_2. Dynamic light scattering measurements of the IP-microgels in aqueous environments show that even in the presence of significant amounts of the ionizable acrylic acid moieties the microgels possess a large swelling response from 300nm in size to approximately 600nm. Two types of nanoparticles of titanium dioxide were immobilized within the microgels - commercially available Degussa particles and fine TiO_2 nanoparticles synthesized by hydrolysis of titanium(IV)isopropoxide. Transmission electron microscopy (TEM) of the composite materials shows that TiO_2 can be successfully incorporated within the microgels and the nanoparticles do not aggregate. Using a simple spectroscopic method based on UV-VIS absorption, the extent of loading of the TiO_2 within the polymeric matrix was found to be as high as 74% by mass.

INTRODUCTION

Composites consisting of inorganic materials dispersed within a polymeric framework offer a versatile avenue to tailor the functional properties of materials. To design advanced functional materials for photocatalysis and other applications, we have focused on composite materials of inorganic nanoparticles such as TiO_2 embedded within microspheres of a responsive polymeric network. TiO_2 forms an n-type semi-conductor, which is sensitive to the UV-Visible spectrum (1). When activated, the surface of a TiO_2 colloid generates short-lived electron-hole pairs that are responsible for catalytic activity (2). Nanoparticles of TiO_2 with vastly increased surface area to volume ratio possess an enhanced reactivity and have significant potential as catalysts in environmental applications (1,3). Currently, a drawback to using TiO_2 nanoparticles for remediation is the lack of an efficient approach to collect the catalyst after remediation. Towards this end, several studies have explored the use of TiO_2 thin films. However, TiO_2 thin films can lead to entrainment of the catalyst over time and can also reduce the available surface area of the nanoparticles.

An alternative approach involves the hybrid materials wherein a three-dimensional porous material entraps the TiO_2 nanoparticles. In this context, we have focused on a porous, three-dimensional, polymeric network of a thermally responsive polymer. Stimuli-responsive polymeric networks of materials such as PNIPAM have attracted increasing attention because of their potential applications in drug delivery, sensors, and chemical separations. Cross-linked, microspherical particles or "microgels" of PNIPAM are of particular interest in many of these applications (4,5). These microgels have a hydrodynamic radius in the 0.2-1μm range and can be easily dispersed in aqueous environments to form transparent solutions. Upon heating past the well-known lower critical solution temperature (LCST) of PNIPAM, the microgels rapidly shrink in size and a turbid, phase separated solution results. In our study, microgels of poly(N-isopropylacrylamide) (PNIPAM) with interpenetrating (IP) linear chains of poly(acrylic acid) (PAAc) were synthesized to promote the incorporation of TiO_2.

We report results with two types of nanoparticles. Commercially available Degussa P25 TiO_2 nanoparticles were used for reasons such as easy availability, excellent known remediation properties, extensively research study and known crystalline structure (6,7). Additionally, ultrafine TiO_2 particles were synthesized by a sol-gel technique (8). Here, the approach for the IP-microgel synthesis is reported as well as characterization of the resulting particle morphologies.

EXPERIMENTAL SECTION

Materials: Unless otherwise noted, all chemicals were purchased from Sigma-Aldrich and Acros Organics and used without further purification. Water used in all synthesis was purified using an EasyPure UV system (Barnstead, IA). A 0.2μm filter incorporated into this system removed particulate matter.

IP-Microgel Synthesis: NIPAM was recrystallized from hexane and dried under vacuum prior to use. PNIPAM microgels were synthesized by surfactant free precipitation polymerization as described elsewhere (9-11). Briefly, radical polymerization of NIPAM using N,N'-methylenebisacrylamide as a cross-linker was initiated using Potassium Persulfate in an aqueous medium at 75°C. The solution was purged with nitrogen gas for 45 mins before polymerization. After polymerization for 4h, the final product was centrifuged and cleaned with deionized water four times. The synthesis of the interpenetrating chains of acrylic acid in the microgels was performed by adapting a procedure reported by Xia and Hu (12). The PNIPAM microgels formed above were mixed with AAc and suspended in water at room temperature. The solution was bubbled with N_2 for 1h to displace dissolved oxygen. The initiator KPS and accelerator N,N,N′,N′-Tetramethylethylenediamine (TEMED) were added and the reaction allowed to proceed for 4 h in an ice bath. The IP-microgels were cleaned in a manner similar to the PNIPAM microgels above.

Fine TiO_2 synthesis: A sol-gel technique was used wherein 3ml of titanium tetraisopropoxide and 0.5ml of 37% v/v HCL were added to 200ml of absolute ethanol at 0°C (8). The resulting suspension was peptized by stirring for an additional 4 hours. The solvent was then removed using a rotary evaporator.

Preparation of composite: Nanoparticles of TiO_2 powder (Degussa P25 grade or the as-synthesized ultrafine TiO_2) were suspended in deionized water. The IP-microgel solution was mixed with the TiO_2 suspension in a 1:10 (volume) solution ration and stirred for 1h. The composite thus formed was collected by centrifuging at 8500rpm for 25mins followed by washing and redispersing in fresh DI water.

Characterization: Microgel sizes and polydispersities were determined via dynamic light scattering using a Malvern Zetasizer Nano-S. Samples were sonicated prior to analysis. A 1ml of the microgel solution was placed into a polystyrene cuvette and allowed to thermally equilibrate at a certain temperature for 10 mins before each set of measurements. Data fitting was done using a multi-modal algorithm supplied by Malvern. The collected correlelograms were fitted to diffusion coefficients and converted to a hydrodynamic diameter (13). Composites of IP-microgels and TiO_2 were examined using TEM to visually determine the extent of TiO_2 loading. A drop of the sample solution was placed on a Formvar-coated Cu TEM grid that was examined using a FEI Morgagni 268D. For a quantitative analysis of TiO_2 loaded in the microgels, the composite that was dried under vacuum was treated with boiling concentrated sulfuric acid and ammonium sulfate. A few drops of 30 wt% H_2O_2 were then added to the cooled solution to oxidize the degraded polymer and then the solution was reheated. An additional amount of H_2O_2 was added to develop the colorless titanyl ion into the intensely yellow colored peroxotitanyl ion TiO_2^{2+}. The peroxotitanyl ion formed shows an absorbance at 410nm that was measured using an Oceanoptic USB2000 UV spectrophotometer. A linear calibration curve between the mass of TiO_2 and absorbance was used to assay the TiO_2 content in the composite (3).

RESULTS AND DISCUSSION

Figure 1 shows a transmission electron micrograph of a sample of the IP-microgel. To clearly visualize the interpenetrating chains of PAAc, the sample was stained using Uranyl Acetate which selectively stains the acrylic acid (14). The dark contrast in the interior of the microspherical particles and the dark spots on the periphery indicate that PAAc constitutes a significant fraction of the polymeric particle. The TEM image also shows that the IP-microgels in the dry state are about 200nm in diameter., which is consistent with the DLS results.

200 nm

Figure 1. TEM image of IP-microgels
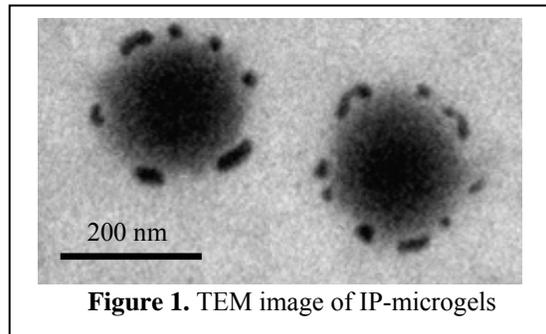
We chose to insert acrylic acid groups within the microgel to enhance the incorporation of TiO_2 in the polymeric matrix. It is known that the carboxylic acid group can functionalize inorganic oxide surfaces. In preliminary experiments we found that when microgels formed from only PNIPAM were used, the TiO_2 nanoparticles were rinsed out during washing of the microgel composites, which indicated that the porous framework of the microgel did not retain the nanoparticles in the absence of any specific interaction with the matrix.

Past reports have shown that incorporation of acrylic acid as a co-monomer with NIPAM to form random P(NIPAM-AAc) copolymers disrupts the hydrophilic/hydrophobic balance of the polymer with the solvent (15,16). This results in a shifting of the volume phase transition of the microgel. Furthermore, the content of AAc in these random copolymer systems has to be limited to a low value as the ionization of the acrylic acid moieties and the resulting charge repulsion between segments can become sufficiently high that microgels of P(NIPAM-AAc) no longer exhibit thermally responsive behavior or shrinking at high temperatures (17-19). By using interpenetrating chains of PAAc, we could maintain the temperature responsiveness and phase transition of PNIPAM microgels while introducing significant amount of carboxylic acid moieties to interact with TiO_2 nanoparticles.

Figure 2 shows the comparison of the volume phase transition with temperature between the IP-microgel and microgels of only PNIPAM. Both polymeric systems transition at roughly 32°C, which is close to the LCST of PNIPAM chains. The two systems also appear to be of similar size before and after transition. This is in contrast to past reports wherein the PAAc chains were used to form an interpenetrating network (IPN) with the PNIPAM network and the resulting IPN microgels were larger in size and also less responsive due to a higher cross-link density (12). In our case, the interpenetrating linear chains of PAAc have not affected the size or the degree of shrinking/swelling of the microgels in water. The inset in Figure 2 shows the appearance of turbidity due to phase separation of the microgels when the sample is heated above the transition region. At room temperature the dispersion of the IP-microgel is transparent.
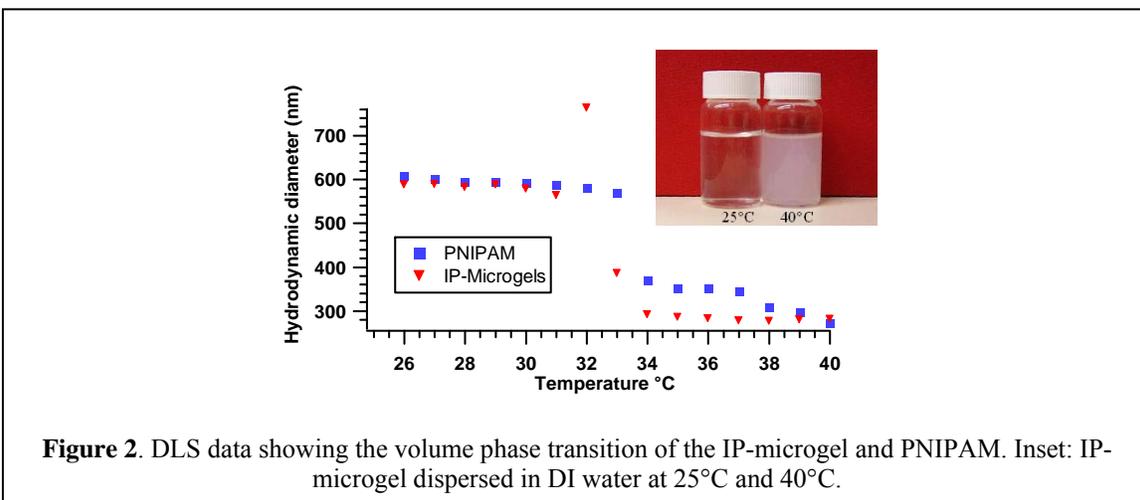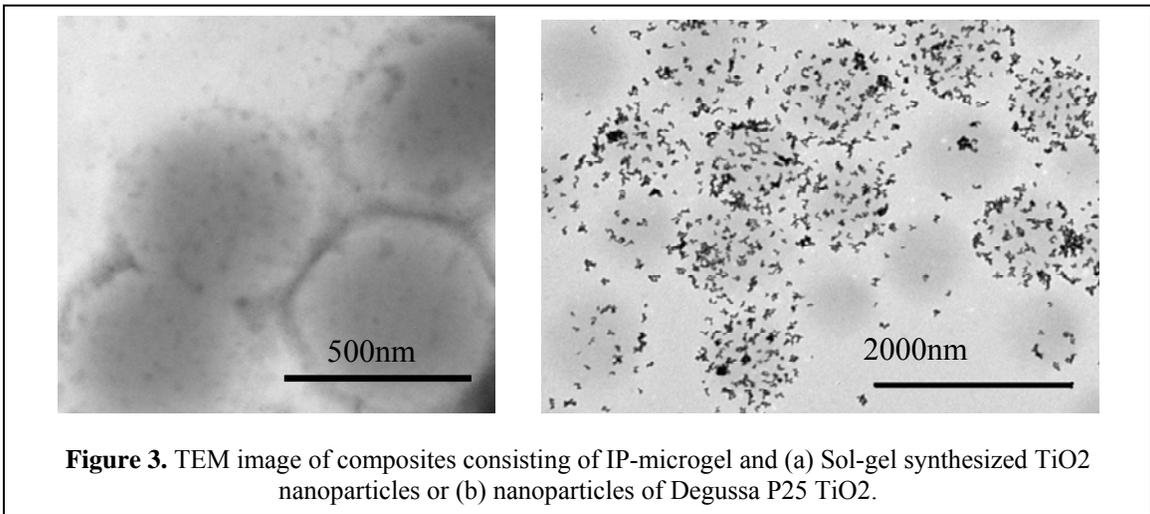

Figure 2. DLS data showing the volume phase transition of the IP-microgel and PNIPAM. Inset: IP-microgel dispersed in DI water at 25°C and 40°C.

Figure 3 shows two types of composites made from the same IP-microgel but with different types of TiO_2. In Figure 3a, the IP-microgels incorporate fine nanoparticles of TiO_2 that were synthesized using a sol-gel technique. The TEM micrograph shows that the TiO_2 particles are roughly 20nm in size. More importantly, the TEM image shows that the TiO_2 particles remain un-aggregated even after the polymer sample has dried and the microgels are in the shrunken state. Figure 3b shows the composites prepared with the commercially available Degussa P25 nanoparticles. The Degussa particles are much larger (~75nm in size) than the sol-gel synthesized TiO_2 but show a similar absence of aggregation. Additionally, due to the higher density of the Degussa P25 nanoparticles, composites made with this grade of TiO_2 settle much easier when centrifuging than composites made with the sol-gel synthesized TiO_2.

Figure 3. TEM image of composites consisting of IP-microgel and (a) Sol-gel synthesized TiO2 nanoparticles or (b) nanoparticles of Degussa P25 TiO2.

UV-Vis Spectroscopy was used to determine a simple colorimetric quantification of the TiO_2 content in polymer-nanoparticle composites. Concentrated sulfuric acid was used to degrade the polymer to carbon and oxidize the TiO_2 into the colorless titanyl ion (TiO_2^+). This titanyl ion complexes strongly with hydrogen peroxide to form a red-yellow suspension which has a characteristic absorbance at 410nm as shown in Figure 4. Using calibration data (not shown), it was determined that the composite formed was 74% TiO_2 weight, which is a significantly high fraction for the inorganic oxide and can be a potential asset in applications.

Figure 4. UV-Vis spectrum for TiO2 quantitative characterization
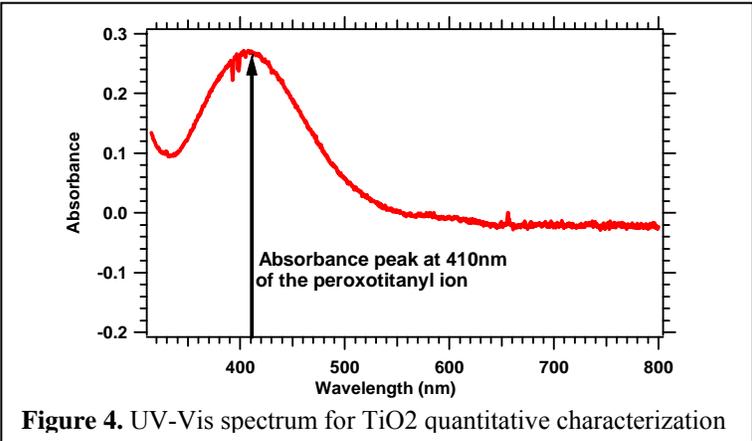
FUTURE WORK

Our future work will focus on testing these composites to determine the efficiency of each approach. It is well known that anatase is the active phase for waste water remediation. Annealing of the synthesized TiO_2 can be done to introduce crystallinity in the fine nanoparticles although this may lead to aggregation. Another route that will be explored is the slow annealing of the TiO_2 particles within the polymeric matrix over time.

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