

Studies in Effect of Methyl Methacrylate to Butylacrylate Ratio on the Properties of TiO₂/poly(methyl methacrylate-co-butylacrylate) Core–Shell Composite Nanoparticles Prepared by Microemulsion Polymerization

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Abstract

Titanium dioxide, as a core, was coupled with the poly(methyl methacrylate-co-butyl acrylate) using amino propyltriethoxy silane as a coupling agent. A two-stage semi-continuous microemulsion polymerization method was used for the synthesis of these core–shell nanoparticles. Ratio of methyl methacrylate to butyl acrylate was varied in the shell of the nanoparticles and the prepared core–shell composite nanoparticles were characterized by Fourier transform infrared spectroscopy, X-ray diffractometer, differential scanning calorimetry, scanning electron microscopy and particle size analyzer along with rheological analysis. It was found that the glass transition temperature and percentage crystallinity decreased whereas the particle size increased with increase in concentration of butyl acrylate in the shell of the core–shell structure.

Keywords: titanium dioxide, amino propyltriethoxy silane, microemulsion polymerization, core–shell nanoparticles, poly(methyl methacrylate-co-butyl acrylate)

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INTRODUCTION

The synthesis of nanoparticle systems consisting of inorganic core and polymeric shell had gathered wide interest in the industry as well as in academia. They offer better mechanical, electrical, thermal and optical properties than its parent components [1]. Methods used for the synthesis of the core–shell nanoparticles include two-step dispersion polymerization method [1], step-by-step method [2], sol–gel method [3], hydrothermal method [4] and microemulsion polymerization method [5, 6]. Microemulsion polymerization is advantageous for preparing thermodynamically stable nano-sized particles, avoiding the chances of any agglomerate formation to happen; also, it is easier to control the particle size of the nanoparticles [7, 8]. This technique had been used to produce core–shell nanoparticles of titanium dioxide (TiO₂) and Silica (SiO₂) [9] having shells of fluorinated acrylics and siliconated polyurethanes [10].

Titanium dioxide is widely used as a photo catalyst and pigment owing to its excellent ultraviolet light scattering ability. Titanium dioxide is comprehensively used in the coating industry on account of its excellent hiding capacity, excellent physicochemical stability, high oxidant affinity, novel optoelectronic property, high refractive index and chemical stability [11–14]. Titanium dioxide is often coupled with an appropriate silane to ensure better compatibility with the polymer matrix [15].

The present study deals with the synthesis of core–shell nanoparticles consisting of titanium dioxide as the core and poly(methyl methacrylate-co-butylacrylate) (poly(MMA-co-BA)) as the shell, coupled with the help of aminopropyltriethoxy silane, by microemulsion polymerization. The ratio of methyl methacrylate (MMA) to butylacrylate (BA) in the shell was varied as 1:1, 1:2, 1:3. The prepared core–shell composite nanoparticles were characterized by Fourier

transform infrared spectroscopy, X-ray diffractometer, differential scanning calorimetry, scanning electron microscopy, particle size analysis and rheological analysis. The mentioned core-shell composite nanoparticles were successfully prepared by microemulsion polymerization method. It was determined that glass transition temperature, crystallinity and viscosity decreased whereas the particle size increased with increase in BA in the poly(MMA-co-BA).

EXPERIMENTAL

Materials

Methyl methacrylate (purity 99%), butyl acrylate (purity 99%), n-pentanol, aminopropyltriethoxy silane, ammonium persulphate, sodium lauryl sulphate, toluene and liquor ammonia (30% conc.) were procured from S. D. Fine Chemicals Ltd., Mumbai, India. Kerr McGee Pigments Ltd., Australia, supplied titanium dioxide (rutile grade). Distilled water was obtained from Bio Lab Diagnostics India Pvt. Ltd., Mumbai, India. All materials were used as obtained without any modification.

Surface Treatment of Titanium Dioxide

Initially, the required amount of aminopropyltriethoxy silane (coupling agent) was charged in a beaker containing 500 mL of toluene. Then, the calculated amount of titanium dioxide (TiO₂:coupling agent = 3:1 w/w) was added to the mixture under continuous stirring (1000 rpm). This mixture was subjected to sonication by the use

of an ultrasound horn (ACE, 22 kHz) for 1 h with 5 s pulse and 2 s relaxation at 40% amplitude. The ultrasonicated mixture was subjected to mechanical stirring at 1800 rpm for 15 h. The modified titanium dioxide particles were filtered and washed. Surface-treated TiO₂ nanoparticles were vacuum dried at 110 °C for 24 h.

Destabilization of MMA and BA

The monomers MMA and BA contain inhibitor, hydroquinone. Hydroquinone stabilizes the monomers as they have the ability to undergo polymerization even at room temperature. In order to remove this inhibitor, the monomers were washed two times with 10% NaOH solution and distilled water.

Preparation of (MMA-co-BA) Pre-emulsion

Weighed quantity of water (20 gm) was charged in a 500-mL beaker to which was added the calculated amount of surfactant (sodium lauryl sulphate; 3% w/w of total quantity of MMA and BA) at high-speed stirring of 1800 rpm. Thereafter, the co-surfactant (n-pentanol; 1% w/w of total quantity of MMA and BA) and total quantity of destabilized monomers (methyl methacrylate and butyl acrylate) were added drop-wise at 1000 rpm. After complete addition of the destabilized monomer, the mixture was stirred continuously for 1.5 h at 1800 rpm, to get a stable pre-emulsion (Table 1).

Table 1: Recipe for the Preparation of Pre-emulsion.

Sr. No.	Ratio of MMA:BA	MMA (gm)	BA (gm)	Water (gm)	Surfactant (gm)	Co-surfactant (gm)	Total batch Size
1.	1:1	26.52	26.52	20	1.58	0.5	75.12
2.	1:2	17.68	35.36	20	1.58	0.5	75.12
3.	1:3	13.26	39.78	20	1.58	0.5	75.12

Preparation of the TiO₂/ MMA-co-BA Core-Shell Nanoparticles

The synthesis of TiO₂/MMA-co-BA core-shell nano particles was carried out by microemulsion polymerization in a four-necked glass reactor equipped with a stirrer, a thermometer, a nitrogen gas inlet and a condenser (fitted with CaCl₂ drying tube). The glass reactor was charged with distilled water (90 gm), core (treated titanium dioxide, MMA-co-BA: TiO₂ = 24:1), surfactant

(sodium lauryl sulphate, 6% w/w of total quantity of MMA and BA), co-surfactant (n-pentanol, 2% w/w of total quantity of MMA and BA) and initiator (ammonium persulphate, 1.1% w/w of total quantity of MMA and BA) in a sequence. Liquid ammonia was added (as required) to maintain the pH in between 7 and 8. 15 wt% of pre-emulsion was added drop-wise to initiate the seed polymerization. The solution was heated to 75 °C to decompose the initiator. The heating

was continued until a slightly bluish tint was observed in the reaction mixture, which indicates formation of oligomeric species in the solution. The remaining (85 wt%) pre-emulsion was then added drop-wise over a period of four hours. After the complete addition of pre-emulsion, the solution was

heated to 80 °C for another one hour. The extent of reaction was analyzed by determining the non-volatile content of the emulsion. Ethanol was used as a de-emulsifier for the purpose. The prepared recipes are listed in Table 2.

Table 2: Recipe for the Preparation of Core-Shell Nanoparticles.

Sr. No.	Ratio of MMA:BA	Pre-emulsion (gm)	Water (gm)	Surfactant (gm)	Co-surfactant (gm)	Initiator (gm)	Treated TiO ₂ (gm)
1.	1:1	75.12	90	3.15	1	0.6	2.21
2.	1:2	75.12	90	3.15	1	0.6	2.21
3.	1:3	75.12	90	3.15	1	0.6	2.21

X-Ray Diffraction (XRD) Analysis

XRD patterns were taken to analyze the percent crystallinity of the prepared core-shell composite nanoparticles on a Rigaku Mini-Flex X-ray Diffractometer. A normal focus copper X-ray tube operated at 30 kV and 15 mA was used for the analysis. Sample scanning was done from 10 to 50 °C at the rate of 3 °C /min. The data processing was done using the Jade 6.0 software.

Differential Scanning Calorimetry (DSC)

DSC analysis was carried out to determine the effect of MMA:BA ratio on the glass transition temperature of the composite nanoparticles. DSC (Q 100 DSC, TA Instruments Ltd., India) characterization was done to investigate the glass transition temperature of the core-shell nanoparticles. Samples were scanned at a scan speed of 10 °C/min and nitrogen purge rate was maintained constant at 50 mL/min.

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR analysis was carried out to analyze the functional groups of MMA, BA and treated TiO₂, in the prepared core-shell composite nanoparticles. The FTIR spectra were recorded using Perkin Elmer Spectrum GX equipment. Samples were scanned with a resolution of 2 cm⁻¹ in the scan range of 450–4000 cm⁻¹.

Table 3: Effect of MMA:BA Ratio on the % Crystallinity Obtained through XRD.

Ratio of MMA:BA	Crystallinity (%)
Standard TiO ₂	45.86
1:1	21.07
1:2	15.98
1:3	13.55

Scanning Electron Microscopy (SEM)

Samples were characterized using SEM to understand the surface morphology of the prepared core-shell nanoparticles. Scanning electron microscopic (SEM) analysis was performed with JEOL 6380 LA (Japan).

Particle Size Analysis

Particle size of the prepared core-shell nanoparticles were estimated by Beakman Coulter N-4 plus submicron particle size analyzer. This was carried out to determine the particle size and particle size distribution of the prepared core-shell nanoparticles.

Rheological Analysis

Rheological behavior of the core-shell emulsion was studied using an Anton Paar MCR 101 series Cone and Plate Rheometer in a shear rate range from 0.1 to 100 s⁻¹ with 0.147 mm gap at room temperature.

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis

The X-ray diffractograms obtained for TiO₂ and various core-shell composite nanoparticles are shown in Figure 1. The values obtained for percentage crystallinity are listed in Table 3.

TiO₂ showed characteristic sharp peaks at 28, 37 and 42 2θ° in its XRD patterns. Peaks at same 2θ° were observed in the diffraction patterns obtained for the core-shell nanoparticles having MMA:BA in ratios of 1:1, 1:2 and 1:3. This proves the presence of nano-TiO₂ in all the samples. However, the

intensity of the peaks decreased with increase in concentration of BA in the shell of the nanoparticles. This happened due to the amorphous nature of BA, increase in which decreased the overall crystallinity of the material.

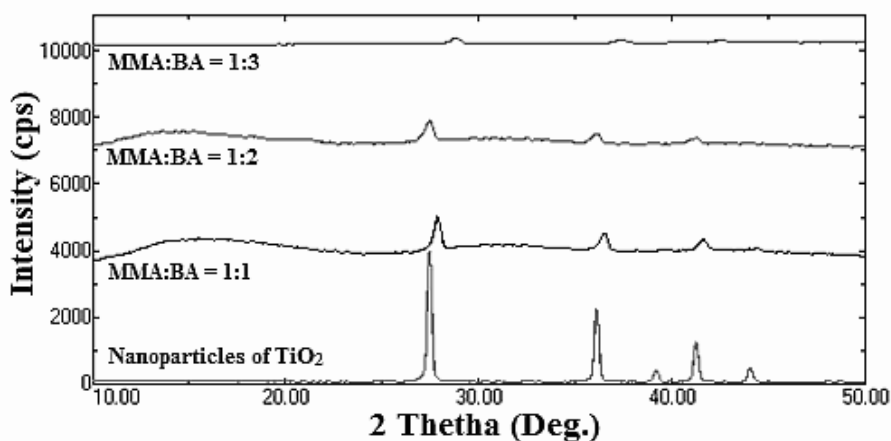


Fig. 1: X-Ray Diffractograms Obtained for TiO₂ Core-Shell Nanoparticles Containing Varying Ratio of MMA:BA.

Percentage crystallinity decreased with increase in BA in the ratio of MMA:BA. Decrease in percentage crystallinity was due to the shell formed onto the surface of the titanium dioxide. Shell was made up of poly(methyl methacrylate) and poly(butyl acrylate), both of which are amorphous as compared to titanium dioxide. However, poly(butyl acrylate) is even more amorphous than poly(methyl methacrylate) due to the longer chain length caused because of butyl group, which decreased the intermolecular

forces of attraction. Thus, as the poly(butyl acrylate) content increased in the shell, amorphous phase increased.

Differential Scanning Calorimetry (DSC)

Poly(methyl methacrylate) and poly(butyl acrylate) are amorphous in nature and, therefore, they possess only glass transition temperature (T_g). T_g values obtained for the core-shell nanoparticles having different ratios of MMA:BA are listed in the DSC curves shown in Figure 2.

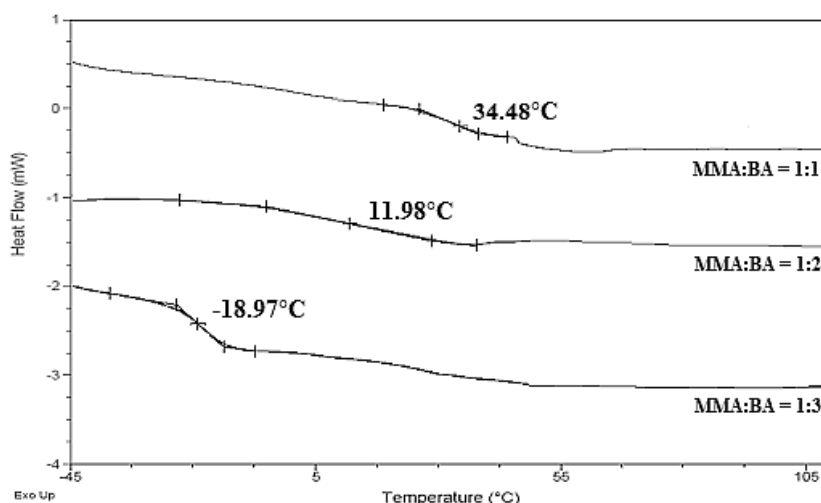


Fig. 2: Glass Transition Temperature Curves Obtained for TiO₂ Core-Shell Nanoparticles Containing Varying Ratio of MMA:BA.

Poly(butyl acrylate) is soft compared to poly(methyl methacrylate) and accordingly they have T_g of -45 and 105 °C respectively. T_{og} of the core-shell nanoparticle decreased with increase in the concentration of BA in the shell. Poly(butyl acrylate) have a longer chain length than poly(methyl methacrylate), caused because of butyl group. So, they have lower intermolecular forces of attraction. As the concentration of poly(butyl acrylate) increased in the shell, amorphous phase increased, increasing the amorphicity of the system.

Thus, the shell became more and more amorphous with the increase in concentration of BA. This made the shell softer decreasing its glass transition temperature.

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra of the aminopropyltriethoxy silane-treated TiO_2 having poly(MMA-co-BA), with varying ratio of MMA:BA, as the shell are shown in Figure 3.

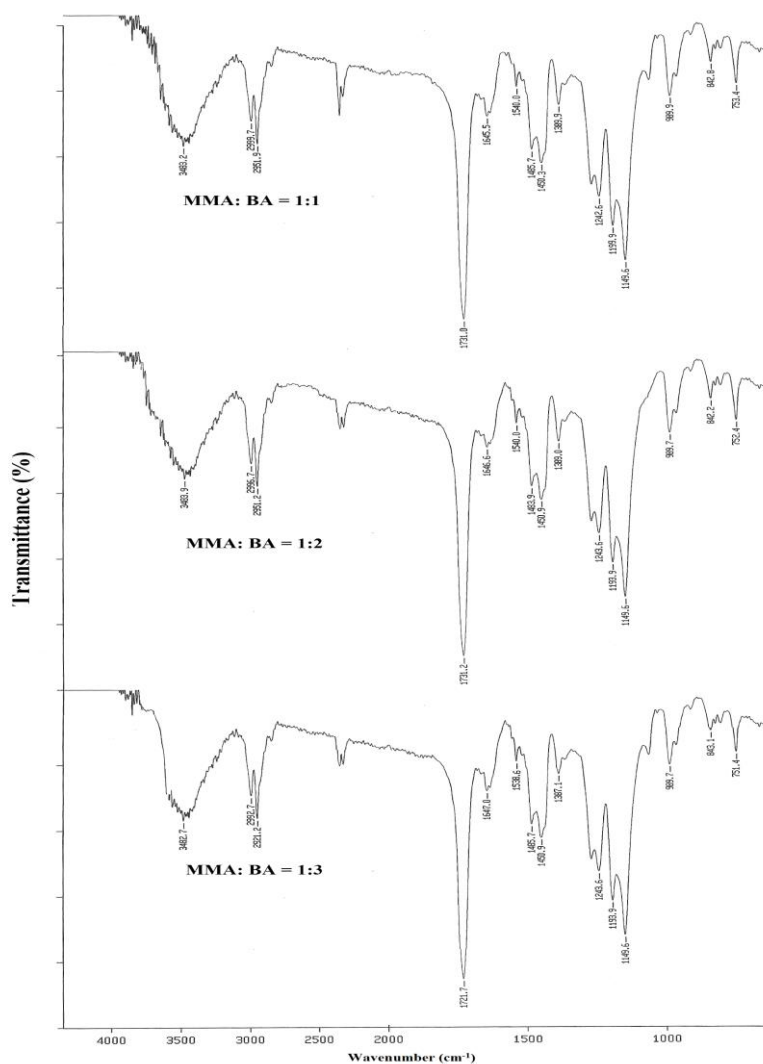


Fig. 3: FT-IR Curves Obtained for TiO_2 Core-Shell Nanoparticles Containing Varying Ratio of MMA:BA.

The vibrational absorption at low wavenumbers such as ~ 750 and ~ 840 cm^{-1} shows the existence of Ti-O-Ti backbone. The peaks around ~ 3400 and ~ 3600 cm^{-1} are the characteristic peaks for the surface hydroxyl groups of TiO_2 . The absorption bands at ~ 1150

and ~ 1240 cm^{-1} are due to the presence of aminopropyltriethoxy silane. The stretching at ~ 1645 and ~ 1730 cm^{-1} shows the presence of C=O in MMA and BA backbone, and aliphatic functional group such as CH_2 . The stretchings at ~ 2950 and ~ 2995 cm^{-1} show the presence of

the methyl group CH_3 . The absorption peak at $\sim 1190\text{ cm}^{-1}$ is caused by the C-O bond vibrations which are present in the backbone of MMA and BA. The stretching at $\sim 3480\text{ cm}^{-1}$ is a characteristic peak of NH_2 , which is present in aminopropyltriethoxy silane. Thus, the FT-IR spectrum proves the presence of TiO_2 , MMA, BA and

aminopropyltriethoxy silane in the prepared nanoparticles.

Particle Size Analysis

Average particle size obtained for the prepared core-shell nanoparticles is listed in Table 4 whereas the particle size distribution curves are shown in Figure 4.

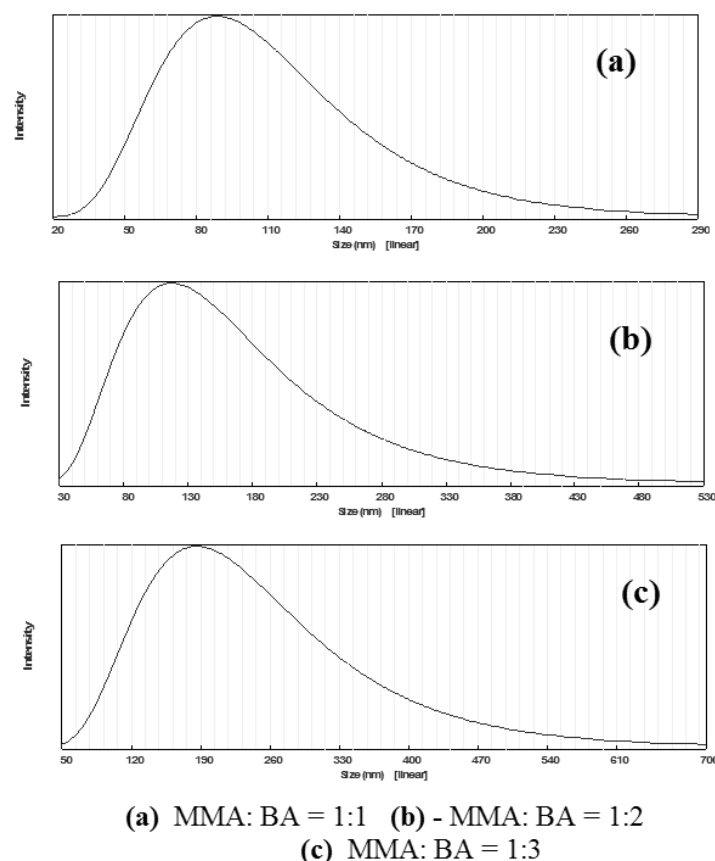


Fig. 4: Particle Size Distribution Curves Obtained for TiO_2 Core-Shell Nanoparticles Containing Varying Ratio of MMA:BA.

Table 4: Effect of MMA:BA Ratio on the Particle Size.

Ratio of MMA:BA	P. D. I.	Average particle size (nm)
1:1	0.097	90.3
1:2	0.165	125.3
1:3	0.357	194.3

It was observed that with the concentration of butyl acrylate increased in the shell, particle size also increased. Intermolecular forces of attraction are less in poly(butyl acrylate) than in poly(methyl methacrylate) due to the presence of butyl group (as compared to methyl in PMMA). Thus, for the same number of molecules, poly(butyl acrylate) will occupy larger volume as compared to poly(methyl methacrylate). PDI also increased with the

increase in BA content in poly(MMA-co-BA). As the concentration of BA increased in poly(MMA-co-BA), the size of the nanoparticle increased erratically affecting its PDI.

Rheological Analysis

Rheology is an important property to understand the stability and flow of the emulsion. Emulsion rheology is often affected

by its chemical composition, polarity of the material and pH. The curves of viscosity (Pa.s) versus shear rate (s^{-1}) obtained for the

prepared core-shell emulsion nanoparticles is shown in Figure 5.

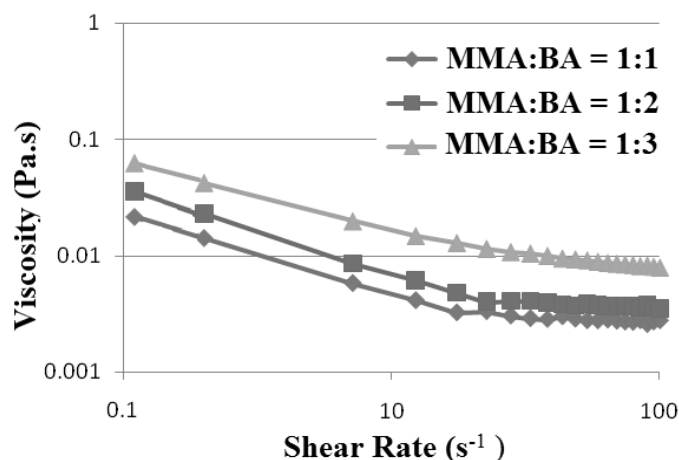


Fig. 5: Graph of Viscosity vs Shear Rate Obtained for TiO_2 Core-Shell Nanoparticles Containing Varying Ratio of MMA:BA.

Prepared emulsions underwent shear thinning with increase in shear rate. Thus, they show thixotropic behavior. Poly(butyl acrylate) has a T_g of $-45\text{ }^\circ\text{C}$ and PMMA has a T_g of $105\text{ }^\circ\text{C}$. The T_g of core-shell polymer shifted towards the T_g of poly(butyl acrylate) with increase in butyl acrylate content, leading to a rubber-like behavior, post polymerization. This rubber like nature increased the viscosity of the material. As butyl acrylate content increased, this rubber nature of the material increased, increasing the viscosity.

Scanning Electron Microscopy (SEM)

Figure 6 shows the scanning electron micrographs obtained for the core shell nanoparticle containing different mole ratios of MMA:BA [1:1 (a), 1:2 (b) and 1:3 (c)]. It can be seen that the particle size increased with the increase in concentration of butyl acrylate. This was the same trend observed in particle size analysis. As the BA content increased, aggregation amongst the particles increased; which was due to sticky nature of poly(butyl acrylate), induced due to lower T_g .

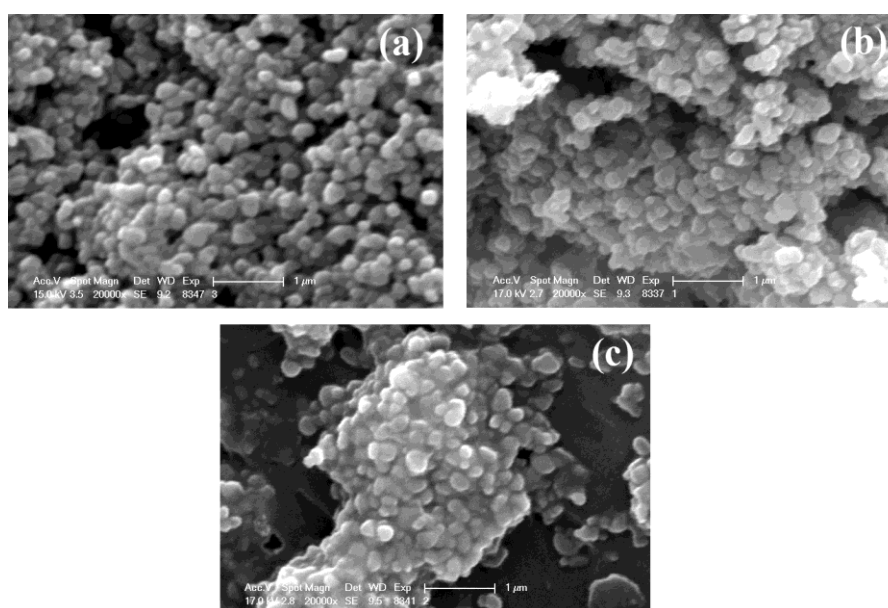


Fig. 6: Scanning Electron Micrographs Obtained for TiO_2 Core-Shell Nanoparticles Containing 1:1 (a), 1:2 (b) and 1:3 (c) Ratio of MMA:BA.

CONCLUSIONS

TiO₂/poly(MMA-co-BA) nanoparticle with core-shell composite structure was successfully synthesized by microemulsion polymerization. This work describes the effect of molar ratio of butyl acrylate to methyl methacrylate on the properties of the microemulsion. FT-IR analysis shows the presence of MMA, BA, TiO₂ and the coupling agent in the core-shell structure. Percentage crystallinity and glass transition temperature decreased with increase in MMA:BA molar ratio. Viscosity increased with increase in MMA:BA mole ratio. From these results, it can be concluded that the mole ratio of MMA:BA had a significant effect on the properties of core-shell nanoparticles prepared via microemulsion polymerization.

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