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ORIGINAL ARTICLE

Fabrication of core/shell hybrid organic–inorganic polymer microspheres via Pickering emulsion polymerization using laponite nanoparticles



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Abstract Oil-in-water (o/w) emulsions of styrene, as monomer oil in water, were achieved successfully via Pickering emulsification with laponite nanoparticles as the sole inorganic stabilizers. The formed emulsions showed excellent stability not only against droplets coalescence (before polymerization) but also against microparticles coagulation (after polymerization). Generally, the number of composite polystyrene microparticles (PS) increased and their sizes decreased with the content of solid nanoparticles used in stabilizing the precursor o/w emulsions. This is consistent with the formation of rigid layer(s) of the inorganic nanoparticles around the PS microparticles thus a better stability was achieved. The composite microparticles were characterized using various techniques such as surface charge, stability, transmission electron microscope (TEM), scanning electron microscope (SEM) and Fourier transform infra-red (FT-IR). Coating films of the prepared latexes were applied to flat glass surfaces and showed reasonable adhesion compared to PS latex particles prepared with conventional surfactants. The effect of employed conditions on the features of the resulting emulsions in terms of stability and particle size has been discussed.

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1. Introduction

The synthesis of structured organic/inorganic hybrid materials is an actual topic of research because they have many potential applications such as delivery systems, photonic crystals, optics, smart microelectronics, smart membranes, separation devices and functional materials (Fang et al., 2009). Hybrid organic–inorganic materials are not simply physical mixtures but they can be broadly defined as molecular or nanocomposites with organic and inorganic components, intimately mixed where at least one of the component domains has a dimension ranging from a few Å to several nanometers. Therefore, they present a combination of the advantageous properties of inorganic nanoparticles and organic or bioorganic materials. Organic/inorganic nanocomposites can be prepared by many methods such as micro-emulsion polymerization, soap-free emulsion polymerization, seeded emulsion polymerization and blending (Palkovits et al., 2005; Lee et al., 2007; Wang et al., 2006; Hwang et al., 2005). It is known that the presence of finely divided solids in processes involving contact of oil and water often results in the formation of solid stabilized emulsions (often referred to as Pickering emulsion). The fine solid powders situated at the surface of droplets form a spherical shell and impede coalescence when two droplets approach each other (Pickering, 1907; Binks and Lumsdon, 2000a; Sullivan and Kilpatrick, 2002; Kahn et al., 2002; Binks, 2002). As the characteristics of Pickering emulsions, the Pickering emulsion polymerization is a feasible way for the preparation of organic (core)/inorganic (shell) hybrid particles or inorganic hollow particles followed by the removal of the template core. It is recognized that the ordinary emulsion route needs relatively large amount of surfactants serving as emulsifiers and recycling the surfactants after polymerization is rather tedious. Pickering emulsion polymerization possesses many advantages including the reduction of foaming problem, lower toxicity and lower cost because of surfactant-free, and so has been extensively studied (Pickering, 1907; Binks and Lumsdon, 2000b,c, 2001; Binks et al., 2002, 2003, 2005, 2010; Binks and Fletcher, 2001; Zhang et al., 2009; Dyab, 2004).

There are several articles that discussed Pickering polymerization using many solid particles such as, nano-SiO₂, TiO₂, Fe₃O₄, CaCO₃, laponite, ZnO and clay. Chen et al. (2008) prepared ZnO/polystyrene composite particles using ZnO nanoparticles as a surfactant and different initiators such as the water-soluble potassium persulfate (KPS) and the oil-soluble 2,2-Azobis(isobutyronitrile) (AIBN) initiator. They also reported that, due to the difference of degree of hydrophilicity, AIBN-initiated system resulted in ZnO-shell and PS-core composite particles while KPS-initiated systems resulted in pure PS particles and composite particles with ZnO on the surface or ZnO embedded inside. Another finding was that the ZnO/PS composite particles showed a good pH adjusting ability and can serve as a potential pH buffering material. Luo et al. (2008) synthesized TiO₂/PS core-shell nanospheres by a novel combination of sol-gel and microwave-assisted emulsion polymerization method. They stated that, the obtained nanoparticles have smooth surfaces and the diameter and its distribution of the nanospheres are related to the concentration of the styrene monomer in the emulsion solution.

Bon et al. (2007) described a simple and effective method for the fabrication of organic–inorganic hybrid hollow spheres by a Pickering emulsion polymerization method, and the use of TiO₂ nanoparticles to form colloidosomes that may be used as the polymerization vessels. This type of hybrid hollow sphere can be used in the fields of drug release systems and photocatalytic applications. For example, a drug or any beneficial agent could be added into the formulation in combination with a monomer or reactive oligomer prior to the scaffolding polymerization process. Zhang et al. (2009) used Pickering emulsion polymerization to prepare PS/nano-SiO₂ composite microspheres by using organically modified nano-SiO₂ particles as stabilizer, the PS/nano-SiO₂ composites with core-shell structure and bare PS spheres were obtained at different synthetic conditions. They found that the particle concentration, particle wettability and pH value of particle dispersion have great effects on the morphologies of PS/nano-SiO₂ composites. The relatively low particle concentration or strong particle hydrophilicity or alkaline particle dispersion favored the formation of nano-sized bare PS spheres. A possible mechanism for the formation of the different morphologic composites was also proposed.

Wang et al. (2009) fabricated nanocomposite microspheres with (PS) cores and shells of Fe₃O₄ nanoparticles by Pickering suspension polymerization of styrene stabilized by Fe₃O₄ nanoparticles which acted as effective stabilizers during polymerization and as building blocks for creating the organic–inorganic hybrid nanocomposite after polymerization. The morphologies of magnetic PS microspheres were tunable and could be controlled via the method(s) by which the original Pickering emulsions were prepared due to their high stabilization during the suspension polymerization procedure.

Interestingly, Chen et al. (2010) synthesized polystyrene/zinc oxide (ZnO) hybrid microcapsules having polystyrene as inner shell and ZnO nanoparticles as outer shell by Pickering emulsion polymerization method. They observed the hollow structure and different morphologies obtained under different conditions by field emission scanning electron microscope. In addition, the photoluminescence property of PS/ZnO hybrid could be maintained without any noticeable variation by comparing to pure ZnO particles.

In this work, we employed laponite as solid inorganic nanoparticles as the sole stabilizing system for a polymerizable oil such as styrene followed by polymerization of the stabilized monomer emulsions to produce a type that may be considered as a fortified emulsion.

2. Experimental

2.1. Materials

Styrene, (C₈H₈), from Alpha Chemika (India), was purified and/or deionized by washing three times with NaOH (10%) aqueous solution with vigorous shaking, carefully removing NaOH solution using separation funnel then the obtained styrene was dried over anhydrous sodium sulfate (Na₂SO₄). Potassium persulfate (KPS), (K₂S₂O₈), from Cambrian chemicals, (purity = 97%). Laponite (RD) was provided by Southern Clay Products Texas, USA. According to the manufacturer, Laponite RD is a fully synthetic clay similar in structure and composition to natural hectorite of the smec-

tite group. It has an empirical formula of $\text{Na}_{0.7}^+ [(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]^{0.7-}$ and a charge deficiency of 0.7 per unit cell. It is comprised of six octahedral magnesium ions sandwiched between two layers of four tetrahedral silicon atoms. Isomorphous substitution of magnesium with lithium in the central sheet creates a net negative charge compensated by intralayer sodium ions located between adjacent layers in a stack. It contains 59.5% SiO_2 , 27.5% MgO , 0.8% LiO , and 2.8% Na_2O and has a specific surface area of $370 \text{ m}^2 \text{ g}^{-1}$ and cationic exchange capacity (CEC) of $7.3 \times 10^{-4} \text{ mol g}^{-1}$. The dimensions of the elementary platelets are the followings: diameter 30 nm and thickness 0.1 nm. In the dry state or in organic solvents, the platelets are pillared up, forming 2–3 layers thick tactoids held together by long-range attractive forces. Reactive silanols, corresponding to structural defects, are located at the broken edges of these stacks while MgOH groups are contained into the internal space of the individual clay sheets. All other chemicals were supplied from El-Nasr Company, Egypt, and used without any further purification.

2.2. Methods

2.2.1. Preparation of o/w emulsion templates stabilized by laponite and subsequent polymerization

O/w emulsion, in which the volume fraction of oil (ϕ_o) equals 0.2, was prepared in a glass reactor by adding 2 cm^3 of monomer oil to 8 cm^3 of pure water containing a known mass of hydrophilic solid nanoparticles (laponite), the mixture was then homogenized, using a Heidolph DIAX homogenizer – made in Germany – rotor-stator with a 18 mm stator diameter head-operating at 23000–26000 rpm for 3 min. The head was immersed in the liquid mixture so that when the rotor blades turn, the liquids were forced between the slits in the stator. Uniform homogenization was achieved by moving the container vertically, the emulsification system is shown schematically in Fig. 1. The continuous phase of the formed emulsions and hence their types were identified by means of the drop test in which a drop of the emulsion was added to about 2 ml of pure oil and pure water phases, respectively. An emulsion which dispersed in the oil phase but not in the aqueous phase was assessed as oil continuous (w/o) and vice versa. For Pickering polymerization step, a known amount of the appropriate initiator was added to its preferable phase (oil or water) then stirred continuously for about 12 h in a water bath maintained at $70\text{--}72^\circ\text{C}$ using stirrer-heater device model ingenieurbüro cat, M.Zipperer GmbH, type: M 601, made in Germany until the latex polymer microparticles are formed.

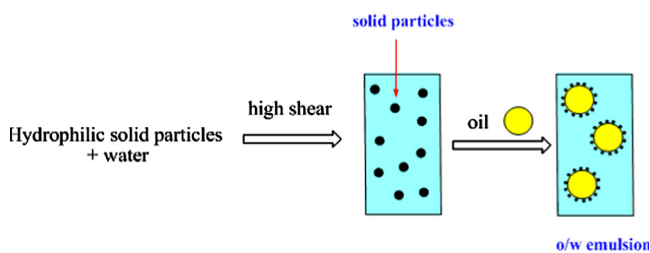


Figure 1 Schematic diagram for preparation of o/w solid particles-stabilized emulsion.

2.3. Characterizations

2.3.1. Conductivity measurements

Conductivity measurements were performed immediately after preparation of the emulsions using a portable conductivity meter (Model CM-1K) from TOA electronics Ltd. Tokyo, Japan, equipped with Pt/Pt black electrodes at room temperature. It was first calibrated with a standard 0.1 M KCl solution and the measurements were reproducible up to $\pm 2.0 \mu\text{S cm}^{-1}$.

2.3.2. Turbidity measurements

Turbidity is due to the presence of suspended latex particles, the presence of these particles changes the optical property of the sample and causes light rays to be scattered and/or absorbed rather than transmitted in straight line through the sample. Therefore, the critical coagulation concentration of solid dispersions (CCC) can be determined. The unit of turbidity is nephelometric turbidity unit (NTU); where nephelometry is used for measuring the scattered light. The values of turbidity were measured using bench turbid meter (Model 1150 ICM), made in USA. Adding few drops of the resulted polymer microparticles into a vessel containing a known amount of an electrolyte like NaCl, CaCl_2 or AlCl_3 at different concentrations in the range of 0.001–1 M, then the turbidity was recorded.

2.3.3. Electron microscopy

Scanning electron microscope (SEM) images were collected by a JOEL JSM-5400 LV electron microscopy (Japan), after the samples were dispersed in absolute ethanol, dried in air, and then coated by gold in JOEL, JES-1100 E Ion Sputtering Device, Japan. Particle or drop size distribution was determined using a Malvern Mastersizer MS20 particle sizer, UK.

2.3.4. Viscosity measurements

Viscosity was measured in cP or mPa s using Brookfield DV-II+ viscometer, from Stoughton, USA, RT 45499 with speed from 0.01 to 200 rpm using S18 spindle type. The viscometer could also provide the relevant shear stress (SS) (dyne/cm^2 or Newton/m^2), shear rate (SR) (1/s) and torque (scale percentage) data.

2.3.5. FT-IR and TGA analyses

Fourier transform infra-red spectra were recorded from 400 to 4000 cm^{-1} on JASCO, FT-IR 6100 (Fourier transform infra-red spectrometer, Japan) under ambient conditions on compressed ground samples with KBr into disks. Typically, 64 scans at a resolution of 4 cm^{-1} were accumulated to obtain one spectrum. Thermogravimetric analysis (TGA) was carried out using a DTG-60H simultaneous DTA-TG analyzer from SHIMADZU-Japan. The measurements were made under oxygen from 0 to 500°C , at a heating rate of 10°C/min .

2.3.6. Film applicator technique for adhesion test

Adhesion of polymer latex microparticles to surfaces was achieved using film applicator technique; its thickness when being wet is 120 micron and 30–50 micron when it was dry. About 1.5 g of the latex microparticles was cast onto a glass surface and dried at room temperature then the film adhesion was simply examined by scratching. The pH was measured

using a pH – meter model 825 MP Fisher Scientific with a saturated KCl glass electrode. The pH meter was calibrated before use with buffer solutions of pH 4, 7 and 10 at 25 °C.

3. Results and discussion

3.1. Polymer microparticles formed with laponite (RD) nanoparticles as stabilizer

In the present work, we used laponite (RD) nanoparticles as a sole stabilizer for oil-water emulsions. The template emulsions used in this work were of the type oil-in-water (o/w) as we dispersed the hydrophilic laponite nanoparticles in the aqueous phase of the emulsions. The type of the resulted emulsions was tested using the drop test: a drop of as-prepared emulsion was added to a volume of pure oil and pure water, respectively. The drops of all the prepared emulsions were dispersed in water and remained as drops in oil, showing that the Pickering emulsions in this work were all of o/w type. Solid particles are held at the oil–water interface by attachment energy (Binks, 2002; Levine et al., 1989):

$$E = \pi R^2 \gamma (1 \pm \cos \theta)^2 \quad (1)$$

where R , γ , θ represent radius of particle, oil–water interfacial tension and contact angle, respectively. The sign in the bracket is positive for the removal of particles into oil and negative for removal into water. Hydrophobic particles form a contact angle higher than 90° and a larger fraction of the particle surface will reside in oil phase other than in water phase, so they normally stabilize w/o emulsions; for hydrophilic particles, with a contact angle less than 90°, o/w emulsions are more probable. An attempt to fabricate hybrid composite particles comprising (PS) as a core with laponite nanoparticles as a stabilizing shell was carried out via emulsion polymerization using KPS as an initiator. The emulsification of styrene as an oil monomer seemed to be easily accomplished as well as their polymer microparticles which ensure the tendency of a finely divided hydrophilic solid laponite nanoparticles to attach onto the interface between two immiscible liquids while keeping contacts with both phases but to different extents. Therefore, it can be liable to achieve the desired emulsification which in this case should not encounter a drop in the system interfacial tension as it is usual for systems involving conventional surfactants (Saleh et al., 2005). Formulations of the prepared samples are summarized in Table 1.

As laponite acted efficiently to obtain stable emulsions even after polymerization as shown in Fig. 2a and b. It was expected that the adsorption of laponite onto the PS particle interfaces while bearing negative charges (between –18 and –45 mV for samples 120–124, respectively) cause repulsion of polymer microparticles willing to come close together, which is a step prior to coagulation process through electrostatic forces. After

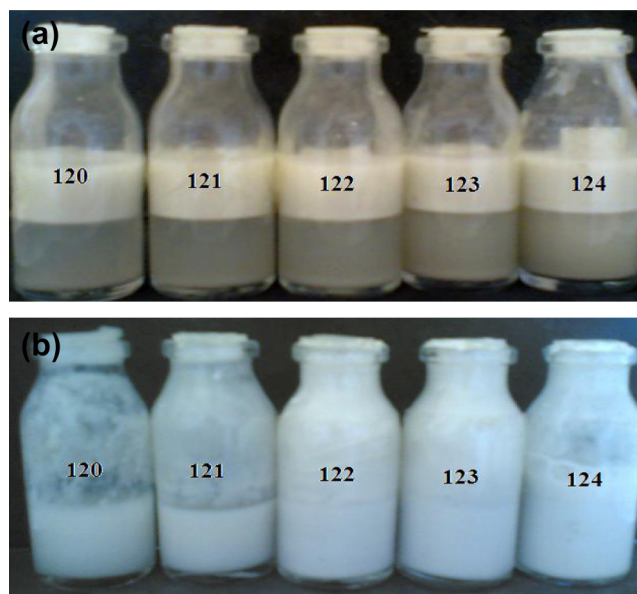


Figure 2 Digital images of (a) the resulted o/w emulsions of styrene stabilized by different concentrations of laponite nanoparticles and (b) the corresponding latex polymers formed after emulsion polymerization process for samples 120–124.

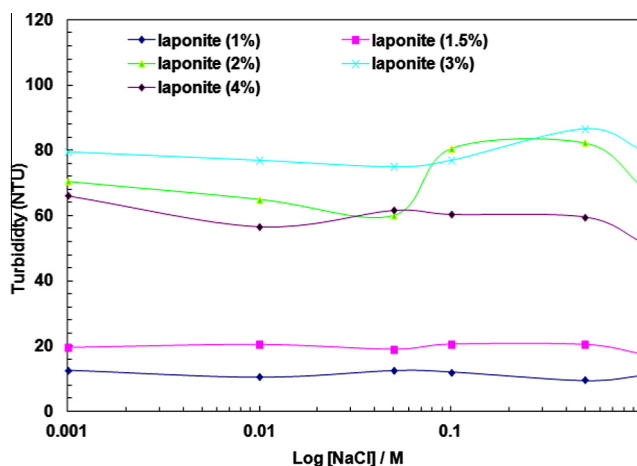


Figure 3 Turbidity of polymer microparticles as a function of NaCl concentration at different wt.% of laponite used in stabilization of the precursor emulsions for samples 120–124.

investigating the coagulation behavior of the produced polymers in the presence of NaCl as an electrolyte, we noticed that the turbidity nearly remained constant up to 1 M NaCl as can be seen in Fig. 3. This means that it was not easy to flocculate

Table 1 Recipes for laponite samples 120–124.

Sample No./composition	120	121	122	123	124
Monomer volume fraction, ϕ_o	0.2	0.2	0.2	0.2	0.2
Laponite (wt.%) based on water	1	1.5	2	3	4
Wt. of laponite, g	0.08	0.12	0.16	0.24	0.32
Wt. of KPS (2%) based on water, g	0.16	0.16	0.16	0.16	0.16

PS microparticles prepared with laponite using NaCl as an electrolyte up to the indicated concentration indicative of high stability for the composite particles. We should distinguish here between the free laponite nanoparticles suspended in the system and those adsorbed onto the PS microparticles interface. We realized that as we increased the laponite concentration from 1 to 4 wt.% in the system, the polymer samples became thicker and we studied this effect further via measuring the viscosity against the concentration of the stabilizer as indicated in Fig. 4.

It is obvious that the viscosity (in cP) has increased significantly when the laponite concentration increased from 1 to 4 wt.%. In addition, the shear rate was constant but accompanied by augmentation in the shear stress value upon increasing the laponite concentration. This is of course a combined contribution of both laponite as rigid solid nanoparticles and the formed PS composite microparticles but all in all it reflects a higher concentration of the formed emulsion hybrid. This can be even more apparent from the torque values of the corresponding samples which elevated more clearly as seen in Fig. 4.

We have investigated the size and surface morphologies of the formed hybrid polymer microparticles using SEM microscopy. Figs. 5 and 6 show the SEM images obtained for laponite based polymer microparticles prepared using 1 and

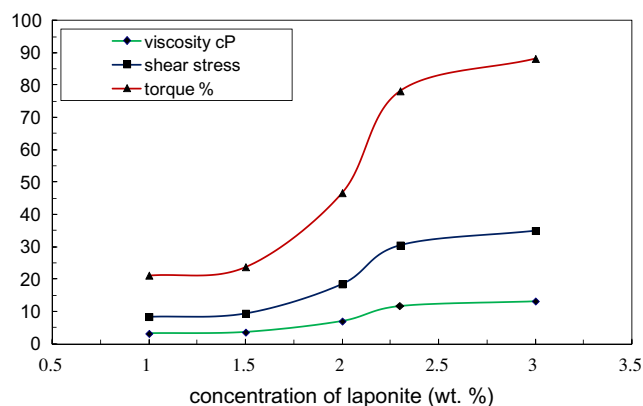


Figure 4 Viscosity, shear stress and torque plots for PS/laponite samples 120–124.

4 wt.% laponite, respectively. It is obvious that in all cases, the obtained composite microparticles having an average diameter ranging from 10 to 40 μm acquired a well-defined spherical shape indicative of a successful emulsification using laponite nanoparticles as a Pickering stabilizer. The nanoparticles of laponite which acted as protective layer(s) against drop coalescence are adsorbed densely on the surface of the formed latex microparticles. Upon increasing the concentration of laponite to 4 wt.% (Fig. 6), it can be noticed that the size of the polymer microparticles became much smaller (around 10 μm in average) while the number of the particles formed was remarkably increased. At higher magnifications, we observed that the concentration of laponite clusters on the surface of the microparticles became more significant compared to microparticles fabricated with lower concentration of laponite nanoparticles (Fig. 5).

The removal of PS core of the polymer microparticles by thermal decomposition was investigated by TGA in air atmosphere as shown in Fig. 7. The figure depicts the TGA of the original laponite sample (a) and for the composite polymer microparticles formed with laponite (b). In the temperature range between 27.85 and 111.46 $^{\circ}\text{C}$, the laponite sample showed a mass loss of approximately 6.202 wt.% due to the evaporation of adsorbed water and the dehydroxylation process. Above 300 $^{\circ}\text{C}$, a steep mass loss was observed which is attributed essentially to the thermal decomposition of polystyrene. No further mass loss was observed at higher temperature and a residue of 29.4% of the initial mass of laponite remained in the composite sample.

In order to verify the formation of laponite shell around the PS core polymer microparticles, we collected the FTIR spectra for a pure laponite sample and for the composite PS/laponite microparticles as depicted in Fig. 8. The composites were dissolved in toluene, followed by centrifugation to separate the PS solution which was diluted into ethanol to precipitate PS. The characteristic bands for laponite were observed at 3549 and 1600 cm^{-1} (OH-stretching of the silicate layer), 1106 cm^{-1} (Si–O – stretching) and 476 cm^{-1} (Si–O – bending). The PS/laponite composite bands at 1650 and 1475 cm^{-1} (C=C aromatic), 1400 cm^{-1} (CH_2 bend) and 760 and 693 cm^{-1} (aromatic CH – stretching out of plane bend) are for PS. In addition, bands between 3070 and 3030 cm^{-1} are for PS (C–H) aromatic stretching and those at 2960–2930 cm^{-1} are for aliphatic (C–H) stretching. It can be clearly seen that the same characteristic peaks of laponite appeared for the PS/laponite composite particles especially at 476 and

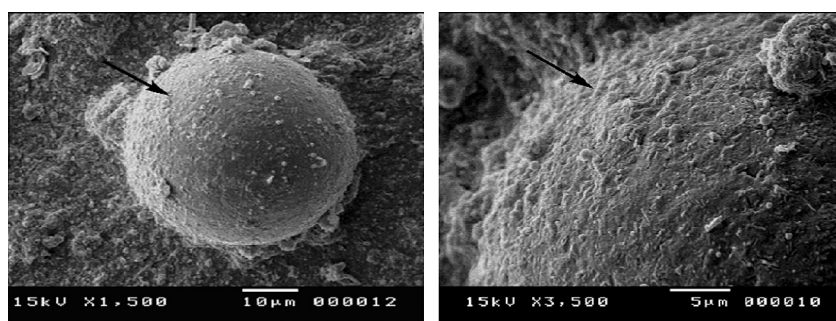


Figure 5 SEM images of PS composite particles prepared with 1 wt.% laponite at different magnifications showing the morphology of the hybrid microparticles interface.

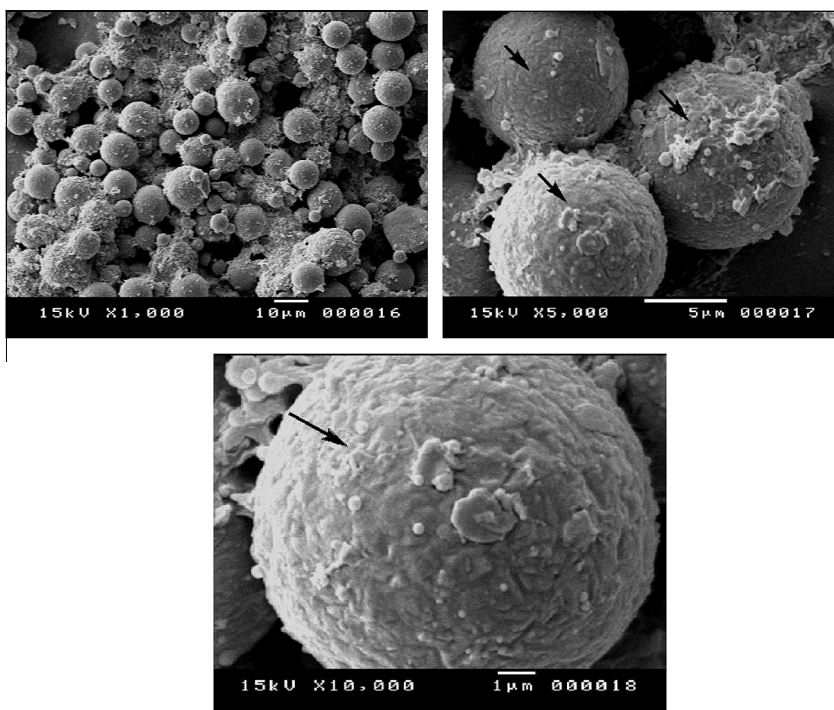


Figure 6 SEM images of PS composite particles prepared with 4 wt.% laponite at different magnifications.

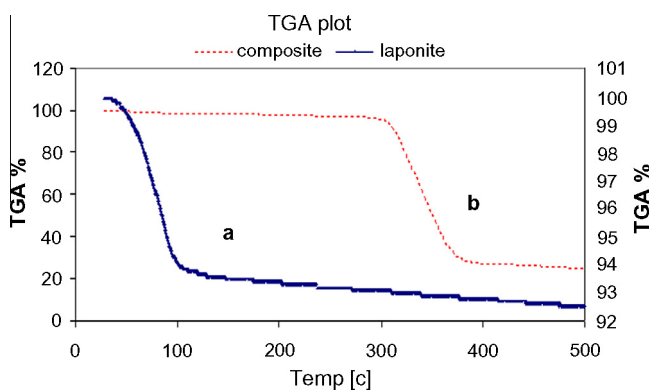


Figure 7 TGA curves of (a) original laponite and (b) PS/laponite composite.

3549 cm^{-1} . This is indicative that the fabricated core/shell composite is made up of PS and laponite.

3.2. Adhesion of PS/laponite composite latex to surfaces

In order to test the adhesion liability of the prepared composite latexes in comparison with latexes prepared using conventional surfactants we applied them to a flat glass surfaces. It was found that the adhesion of the conventional polystyrene (PS) latex fabricated using conventional surfactants like SDS or Hitenol was very poor on the glass surface (Fig. 9). This might be attributed to the low electrostatic charge remaining on the polymer particles prepared with surfactant after washing the polymer with alcohol and water which resulted in more aggregated particles and low adhesion properties.

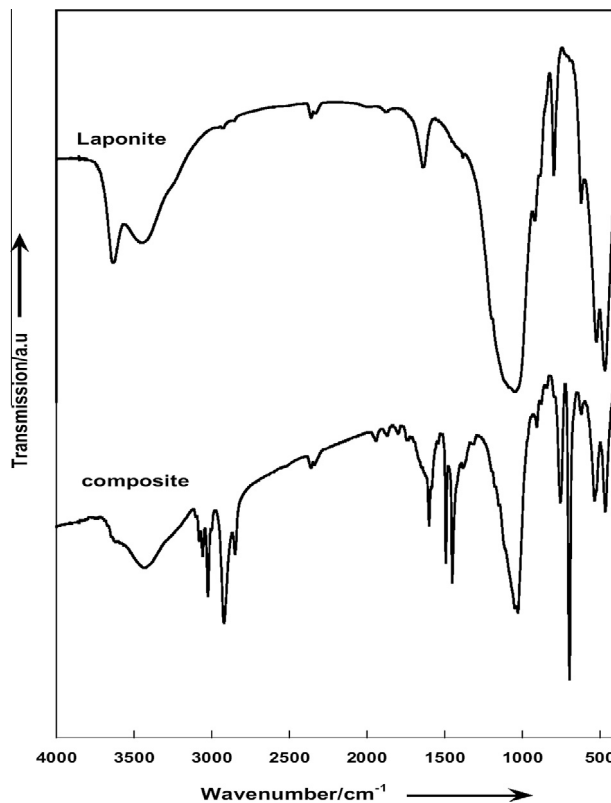


Figure 8 FT-IR plot of pure laponite and PS/laponite composite particles.

Upon using laponite as a sole stabilizer instead of the conventional surfactants such as SDS or Hitenol, we found that

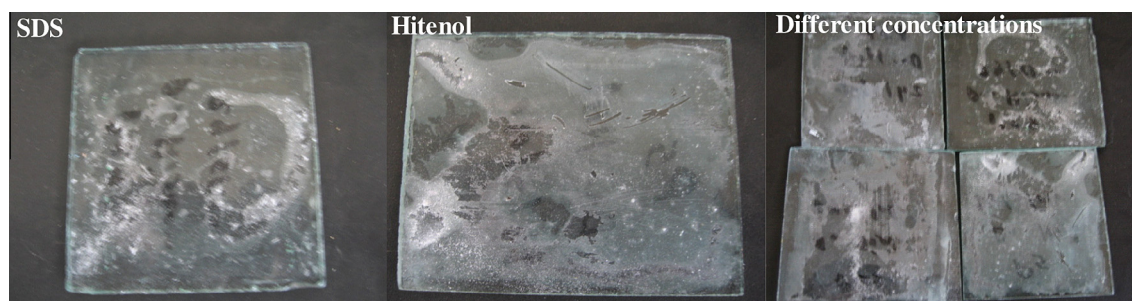


Figure 9 Adhesion of PS latex particles prepared using normal surfactants on glass surface.

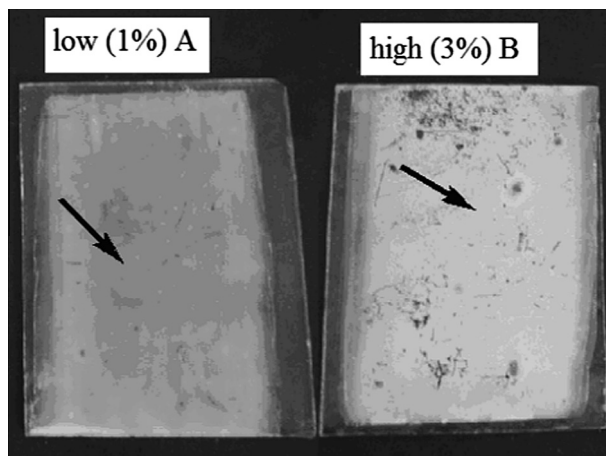


Figure 10 Adhesion of PS latexes prepared using (A) low, (B) high concentration of laponite as stabilizer.

the adhesion was good at low concentration of laponite (1 wt.%) (Fig. 10A) while the situation worsened at high concentration of 3 wt.% (Fig. 10B) indicative of more aggregation took place at high stabilizer concentrations. This may be achieved in another way if we consider that laponite can form hydrogen bonding leading to these aggregations while at low concentration the situation was different which can be accounted for by the participation and contribution of the laponite hydroxyl groups on the surface in the adhesion process to the glass substrates. The adhesion strength may be attributed mainly to van der Waals interactions with no indications of large scale covalent bonding between the polymer composite and the glass surface. The interaction strength and affinity of the polymer particles to the glass surface is dominated by hydrophobic/hydrophilic interactions and hydrogen bonds between side groups of the laponite and the hydroxyl groups on the clean hydrophilic glass plates. Generally, clay minerals, as a layered silicate, contain active sites such as hydroxyl groups, Lewis and Brönsted acidity and are also characterized by the presence of exchangeable metal cations such as Na^+ , Li^+ , Ca^{2+} , etc. located in the spacing between the negatively charged layers. Consequently, organic cations can be electrostatically attached onto clay surfaces by a cation exchange process. In addition to exchangeable cations, the presence of OH groups at the broken edges of the clay platelets, also offers an easy route to accommodate entities with specific functionalities on the clay surface to enhance the coating process.

4. Conclusion

We showed in this study that laponite (RD) nanoparticles can be used as an effective inorganic stabilizer, compared to conventional surfactants, to successfully prepare stable o/w emulsions of styrene, as polymerizable oil in water via Pickering emulsification. The resulted laponite stabilized o/w emulsions showed excellent stability not only against the coalescence (before polymerization) but also against coagulation (after polymerization). The number of formed composite microparticles after polymerization increased while corresponding sizes decreased with the content of laponite nanoparticles used. This could be ascribed to a formation of rigid layer(s) of laponite nanoparticles around the PS microparticles thus preventing coalescence and consequently a better stability of the resulting polymer microparticles against coagulation was achieved. The formed composite latex microparticles can be used in coating formulations on surfaces such as glass and their satisfactorily good adhesion as compared to PS latex prepared with SDS or Hitenol as conventional surfactants was attributed to real participation in the adhesion process through hydroxyl groups on the laponite surface via at least hydrogen bonding.

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References

- Binks, B.P., 2002. *Curr. Opin. Colloid Interface Sci.* 7, 21.
- Binks, B.P., Fletcher, P.D.I., 2001. *Langmuir* 17, 4708.
- Binks, B.P., Lumsdon, S.O., 2000a. *Langmuir* 16, 8622.
- Binks, B.P., Lumsdon, S.O., 2000b. *Langmuir* 16, 3748.
- Binks, B.P., Lumsdon, S.O., 2000c. *Langmuir* 16, 2539.
- Binks, B.P., Lumsdon, S.O., 2001. *Langmuir* 17, 4540.
- Binks, B.P., Dyab, A.K.F., Fletcher, P.D.I., 2002. *Proceedings of 3rd World Congress on Emulsions, Lyon, CME, Paris*, pp. 1–10.
- Binks, B.P., Clint, J.H., Dyab, A.K.F., Fletcher, P.D.I., Kirkland, M., Whitby, C.P., 2003. *Langmuir* 19, 8888.
- Binks, B.P., Philip, J., Rodrigues, J.A., 2005. *Langmuir* 21, 3296.
- Binks, B.P., Dyab, A.K.F., Fletcher, P.D.I., Barthel, H., 2010. *Multiple emulsions*. US patent publication, US 7722891 B2.
- Bon, S.A.F., Chen, T., Colver, P.J., 2007. *Adv. Mater.* 19, 2286.
- Chen, J.H., Cheng, C.Y., Chiu, W.Y., Lee, C.F., Liang, N.Y., 2008. *Eur. Polym. J.* 44, 3271.
- Chen, W., Liu, X., Liu, Y., Kim, H.I., 2010. *Colloid Polym. Sci.* 288, 1393.

- Dyab, A.K.F., 2004. Nanoparticles as Emulsion Stabilizers and their Behavior at Liquid–Liquid Interfaces, PhD Thesis, University of Hull.
- Fang, F.F., Kim, J.H., Choi, H.J., Kim, C.A., 2009. *Colloid Polym. Sci.* 287, 745.
- Hwang, S., Hahn, Y., Nahm, K., Lee, Y., 2005. *Colloids Surf. A* 259, 63.
- Kahn, J.G., Schmitt, V., Binks, B.P., Calderon, F.L., 2002. *Langmuir* 18, 2515.
- Lee, J., Hong, C.K., Choe, S., Shima, S.E., 2007. *J. Colloid Interface Sci.* 310, 112.
- Levine, S., Bowen, B.D., Partridge, S.J., 1989. *Colloids Surf. A* 38, 325.
- Luo, H.L., Sheng, J., Wan, Y.Z., 2008. *Mater. Lett.* 62, 37.
- Palkovits, R., Althues, H., Ruplecker, A., Tesche, B., Dreier, A., Holle, U., Fink, G., Cheng, C.H., Shantz, D.F., Kaskel, S., 2005. *Langmuir* 21, 6048.
- Pickering, S., 1907. *J. Chem. Soc.* 91, 2021.
- Saleh, N., Sarbu, T., Sirk, K., Lowry, G.V., Matyaszewski, K., Tilton, R.D., 2005. *Langmuir* 21, 9873.
- Sullivan, A.P., Kilpatrick, P.K., 2002. *Ind. Eng. Chem. Res.* 41, 3389.
- Wang, T., Wang, M., Zhang, Z., Ge, X., Fang, Y., 2006. *Mater. Lett.*, 2544.
- Wang, C., Zhang, C., Li, Y., Chen, Y., Tong, Z., 2009. *React. Funct. Polym.* 69, 750.
- Zhang, K., Wu, W., Meng, H., Guo, K., Chen, J.F., 2009. *Powder Technol.* 190, 393.