Synthesis of High Solid Content Polyacrylate/Nanosilica Latexes via Miniemulsion Polymerization

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A B S T R A C T

High solid content nanocomposites based on poly(methyl methacrylate-co-butyl acrylate)/nanosilica was synthesized via miniemulsion polymerization in a semi-continuous operation. Oleic acid was used to act as a coupling agent between silica surfaces and polymer. Latexes with solid content of 42% were obtained, containing 5% by weight nano-SiO₂ with respect to polymer. FTIR Results show the modified structure of silica with oleic acid and confirm the presence and bonding of modified silica on the polymer structure. Morphological investigations were performed using TEM analysis. The results of microscopic images confirm the nanocomposite structure where the nanoparticles of silica are coated with the polymer nanolayers. Thermal analysis including DSC and TG/DTA was used to investigate T_g, thermal stability and thermal decomposition of the samples. The nanocomposite latex is compared with the neat latex of the same monomer structure. The results of DTA analysis show an increase of about 8°C in the degradation temperature. DSC Analysis shows that the glass transition temperature of the nanocomposite is higher than that of pure acrylic latex. Moreover, the samples with improved hardness are compared with blank latex sample. All analyses demonstrate the well located silica nanoparticles inside the latex polymeric structure.

INTRODUCTION

Organic-inorganic nanocomposites for whole range of modified properties are very interesting and promising set of materials with their potential use in many fields of applications.

Chau et al. [1] reported some modified coating properties such as hardness and other mechanical properties of a nonocomposite consisting of silica/PMMA prepared just by simple blending of these two components. Similar procedure has been reported by Katsikis et al. [2].

The preparation of organic-inorganic nano hybrids in an emulsion form is much preferable because of its easy processability [3,4]. In coating and adhesive applications, emulsion polymerization is the best route to produce waterborne nanocomposites especially based on acrylic or styrenic polymers. However, other polymerization methods like,
solution, suspension or dispersion polymerization have been reported to produce specifically desired nanocomposites [5-8]. More recently, Ji et al. [9] applied different polymerization methods of distillation precipitation to prepare polymer/silica/polymer tri-layer nanocomposites.

Some researchers have focused on the morphological aspects of these types of nanocomposites [10,11]. Ding et al. [12,13] have prepared two series of nanocomposites of two different polymers of styrene and acrylates containing nanosilica. For the first time, they used oleic acid for modification of silica followed by direct grafting of polymer chains onto the modified surfaces. Their works similar to many other researchers led to a much diluted latex with the solid content below 20%. For example, Bouanani et al. [14] prepared a nanocomposite of encapsulated montmorillonite, where the solid content of product was about 21%. Chen et al. [15] synthesized hybrid latex based on PMMA/SiO₂ with the total solid content under 20%. Similar diluted hybrid latex was presented by Luna Xavier et al. in 2002 [16]. Encapsulation of TiO₂ particles with polystyrene has been performed in a dilute system by Erdem et al. [17]. Mahdavian et al. [18,19] prepared two different systems of nanocomposite latex with 80% of water based on total weight of latex. Recently some workers have presented different methods for preparation of polyacrylate/silica nanocomposites in a dilute scale [20-23]. Similarly, emulsion nanocomposites prepared by Qu et al. [24] and Wen et al. [25] have solid content of about 20%. Zhang et al. [26] prepared monodispersed silica-polymer nanocomposite latex with total polymer content of less than 5%. Kang et al. [27] used special coupling agents to produce acrylate polymer/silica composite via soap-free emulsion polymerization. Reported solid content of their product is 10%. Lately, polystyrene/carbon nanotube composites with a solid content of about 15% are prepared by emulsion polymerization [28]. These solid contents are not suitable for industrial applications where the preferable scale is higher than 40%.

More recently, Diaconu et al. [29] and Wu et al. [30] have developed an approach based on the semi-batch emulsion polymerization method to synthesize high solid content nanocomposites of acrylate polymer and montmorillonite. Meanwhile, miniemulsion polymerization has been developed in recent years to encapsulate inorganic particles because of its distinct aspect of monomer droplet nucleation, which provides advantages for encapsulation of inorganic solids [17,22].

In the present work, a high solid content nanocomposite based on poly(methyl methacrylate-co-butyl acrylate) and silica has been synthesized via miniemulsion polymerization of acrylate monomers in the presence of modified nanoparticles of silica. Oleic acid has been used to act as a coupling agent between the silica surfaces and polymer.

For comparison, blank acrylic latex without nanosilica with the same solid content via similar synthetic procedure has been prepared. An assumption was made that by the performance of an in situ polymerization, nanoparticle coalescence would be reduced because the polymerization taking place in compartmentalized reactors of nanometric dimensions of 50-500 nm. Therefore, miniemulsion process would permit the preparation of nanocomposites with maximum nanoparticle dispersion. The resulting nanocomposites (NA) have been characterized by FTIR, TEM, DSC, TG, DTA and DLS techniques. The analysis shows the presence of nanosilica particles in nanocomposite structure of acrylic latex with high solid content, which likely leads to more efficient thermomechanical properties for these types of resins. Furthermore, different properties of nanocomposite are discussed in comparison to the neat latex.

**EXPERIMENTAL**

**Materials**

In this work, the colloidal nano-SiO₂ having specific area of 230 m²·g⁻¹ with commercial name of Ludox AS-30 were purchased from Sigma-Aldrich, and the industrial grades of methyl methacrylate (MMA), butyl acrylate (BA) and acrylic acid (AA) were applied as received. Potassium persulphate (KPS) from Merck and cetyl alcohol (CA), sodium dodecyl sulphate (SDS), nonylphenol polyethylene glycol ether as a non-ionic surfactant and ammonia, all of
analytical grades have been used.

Preparation of Poly(methyl methacrylate-co-butyl acrylate)/Silica Nanocomposites

Modification of Nano-SiO$_2$ Particles

Oleic acid was used to modify SiO$_2$ particles as they bond to the silanol groups at the surface of nano-sized silica with the hydrogen bonds as illustrated by Ding et al. [12].

In a typical procedure, oleic acid with the weight proportion of 10-20% (related to the pure silica content) was added to colloidal nanosilica dispersion under agitation. After 2 h homogenization with magnetic stirrer, to adjust the pH to a definite value of 5, aqueous ammonia solution (25% by weight) was added dropwise to this dispersion and left under agitation for 24 h at room temperature. In order to remove the excess amount of oleic acid, 25 mL of 1/1 ethanol/water solution was added to the colloidal silica/oleic acid dispersion. Then, the mixture was centrifuged three times (2500 rpm) for 30 min, and after each time, the obtained precipitates were washed with 1/1 ethanol/water (V/V) solution. The resulting precipitates which were modified colloidal nanosilica, without any post-drying were applied to produce the nanocomposites.

Preparation of Miniemulsions

The non-aqueous phase was prepared by dispersing definite quantities of cetyl alcohol and non-ionic emulsifier in the monomer mixture. Note that in this work, a high quantity of nonylphenol polyethylene glycol ether was used because a non-ionic emulsifier could act as a hydrophobe in miniemulsion polymerization [31] and also perform as a coupling agent between the silica surfaces and monomers [11,16].

The modified colloidal silica and ionic emulsifier (SDS) were added into the de-ionized water. The mixture of oil-base and aqueous phase was stirred for 1 h with a mechanical stirrer, followed by ultrasonication with a highly efficient sonifier (Ultraschall prozessor- up 200s- Dr Hielscher) for about 15 min with 150 Watt power. During ultrasonication, the mixture was cooled in an ice-bath to avoid polymerization through homogenization. This procedure resulted in a stable O/W miniemulsion.

Synthesis

The miniemulsion prepared in the previous stage was polymerized by semi-batch emulsion copolymerization in a 1 L five-necked glass reactor, which was equipped with a jacket, reflux condenser, a thermometer, a mechanical stirrer with a stainless steel anchor device, a dropping funnel, and a nitrogen gas inlet.

First, the reaction vessel was charged with a definite amount of distilled water, degassed with nitrogen for about 15 min. A portion of the prepared miniemulsion was discharged into the reactor, allowed degassing in order to remove oxygen for more than 15 min and the remaining portions were charged into a dropping funnel. The initiator (KPS) was dissolved in a definite amount of distilled water and it was added to start the polymerization reaction. The initial charge (150 mL) was stirred at 330 rpm and heated to 75°C to polymerize during 45 min. Afterwards, the remaining part of oil/water base mixture was re-sonicated for 5 min to secure a well nanodispersed miniemulsion, and then it was fed into the reactor with constant flow rate (about 4.5 mL/min) slow enough to achieve monomer starved conditions. In order to complete polymerization, at the end of feeding, the content of reactor was stirred for an additional 2-3 h. The temperature was fixed on 75°C during the reaction with total reaction time of about 3 h.

Then, the system was cooled to room temperature and the final latex was obtained without any post preparative treatments.

Similar procedure was also applied for preparation of pure acrylic latex (A) as a reference sample. Tables 1 and 2 show detailed recipes of samples preparation. It should be noted that Table 1 presents the best procedure and recipe for preparation of nanocomposites where at the end of polymerization and filtering of latex, no coagulation was observed.

Characterization

Overall, the total conversion was followed by gravimetric determination of solid content. The samples taken from the reactor were placed into pre-weighed aluminium plates and short-stopped with about 2 mL of hydroquinone solution of 5% by weight concentration. The overall conversion was estimated...
by division of the experimental solid content into the theoretical solid content. The solid content of the prepared nanocomposites was about 43% and overall conversion was 95%. This conversion level is well higher than those obtained by Qi et al. [22,23] in which similar miniemulsion polymerization carried out.

Infrared spectra of the samples were obtained by a Perkin Elmer Fourier transform infrared spectroscopy from 4000 to 450 cm\(^{-1}\).

A transmission electron microscope (TEM Zeiss Company, CEM902A) was used to observe the morphology of nanocomposites.

Differential scanning calorimetry (DSC) was carried out on a DSC-Raman Hyphenation set (Perkin Elmer, US). The samples were quickly heated to 100°C and equilibrated at that temperature for 3 min, and then cooled to -20°C under nitrogen atmosphere.

Thermogravimetric analysis (TG/DTA) was carried out on Pyrif diamond (SII) (Perkin Elmer, US) in nitrogen atmosphere. The rate of heating was 10°C/min.

**RESULTS AND DISCUSSION**

**FTIR Analysis**

As stated previously, oleic acid was used as a coupling agent between silica surfaces and polymer. This acid modified the nanosilica surfaces via electrostatic interactions and hydrogen bond formation [18].

Particles size distribution was determined by dynamic light scattering with instrument of Mastersizer 2000 (Malvern Instruments Ltd., UK, model: 11029). For this analysis, a fraction of latex sample was diluted with de-ionized water. The reported particle size distribution values represent an average of three repeated measurements.

Pendulum hardness was measured according to the Konig method (ASTM D 4366) using a pendulum hardness tester (Ref. 707PK, Sheen Instruments Ltd.) at 22°C.

**Table 2.** Recipe used for preparation of neat acrylic latex (A).

<table>
<thead>
<tr>
<th>Components</th>
<th>Weight or volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dodecyl sulphate (SDS)</td>
<td>5 g</td>
</tr>
<tr>
<td>Methyl methacrylate (MMA)</td>
<td>180 mL</td>
</tr>
<tr>
<td>Butyl acrylate (BA)</td>
<td>178 mL</td>
</tr>
<tr>
<td>Acrylic acid (AA)</td>
<td>4 mL</td>
</tr>
<tr>
<td>Water</td>
<td>461 mL</td>
</tr>
<tr>
<td>Potassium persulphate (KPS)</td>
<td>1 g</td>
</tr>
</tbody>
</table>

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Figures 1a to 1c show the FTIR spectra of unmodified silica, oleic acid and modified silica with oleic acid, respectively. The spectrum in Figure 1c has been obtained after sample washing with the aqueous solution of ethanol to make sure that there is no unreacted oleic acid in the dried samples. In spectra (a) and (c) the pronounced broad band appears around 1100 cm\(^{-1}\) together with the band at 800 cm\(^{-1}\), which correspond to the vibration absorption of Si-O-Si groups of silica.

Comparing the three spectra in Figure 1 clearly shows the modified structure of silica with oleic acid.
Figure 1. FTIR Spectra of: (a) silica, (b) oleic acid, and (c) modified silica with oleic acid.

The presence of newly appeared peaks of 2920 and 1717 cm\(^{-1}\) in the spectra of modified silica with oleic acid (Figure 1c) confirms the absorption of oleic acid on silica particles.

Figure 2 compares clearly the structure of nanocomposite sample with the pure acrylate polymer as a reference material. The new and intensive peaks in the lower curve confirm the presence and bonding of the modified silica on the polymer structure. In the spectrum belonging to the nanocomposite (lower curve), the adsorption peaks of 1145 cm\(^{-1}\) and 810 cm\(^{-1}\) belong to the extending vibration of Si-O-Si groups. The absorption peak of 3400 cm\(^{-1}\) was affected by extension vibration of Si-OH [20]. The adsorption at 1145 cm\(^{-1}\) corresponding to Si-O-C also confirms that the nanosilica particles have been encapsulated by the polymer [12,13].

Morphological Studies

TEM Photograph visualized the morphology of nanocomposites and the distribution feature of silica particles in the polymer.

Figure 3 displays the TEM image of nanoparticles. Due to the fact that the nano-SiO\(_2\) is less transparent towards electron beam compared to the polymeric materials, the nanosilica appears black or dark gray. It is clear that silica beads (in dark) are surrounded by a thin layer of acrylic polymer (in gray). The polymeric layer is formed via mini-emulsion polymerization of acrylic monomers in presence of modified silica. The layer thickness is nearly 70 nanometers. This morphology formation is represented schematically in Figure 4.

The particle size distribution evaluated by dynamic light scattering is in accordance with these images and it is discussed in the following section.

Figure 3. TEM Image of polymer encapsulated nanosilica.
Figure 4. Schematic diagram of formation mechanism of nanocomposite particles.

Thermal Analysis

DSC

Figure 5 displays the DSC thermogram of a pure acrylic latex and acrylate/silica nanocomposite synthesized via miniemulsion polymerization. As it may be observed in this figure, the glass transition temperature of the nanocomposite (T_g = 26°C) is higher than that of the pure acrylic latex (T_g = 13°C). This may be attributed to the efficiently incorporated nanosilica onto polymer molecules which finally leads to the suppression of molecular movement of the polyacrylate. Furthermore, in this study oleic acid acted as coupling agent between the acrylate polymer and silica that enhanced the adhesion between these two components. Therefore, T_g increased by restricted polymer chain mobility as the polymer interacted with the modified nanosilica.

Zhu et al. [7] reported the similar observation for the nanocomposites based on silica prepared via suspension-dispersion polymerization. They illustrated that the interaction of polymer chains with nanosilica reduces the mobility of polymer chains and leads to the formation of immobilized and restricted mobility regions around the filler particles.

Higher T_g of nanocomposites vis-a-vis of neat polymer component has been observed in different systems [1,20]. However, considering probable variation of molecular weight in the case of synthesized nanocomposites, any suggestion for the changing T_g is doubtful.

TG/DTA

Before the thermogravimetric analysis of the test samples, free dispersed silica was separated from the composite particles in the latex. The method was based on coagulation of latex sample with concentric sulphuric acid, washing with distilled water several times and filtered with the help of centrifugation. Then, the sample was dried at 60°C for two days.

Figure 6 shows the TG/DTA thermograms of pure acrylic latex (A) and acrylate/silica nanocomposite synthesized by miniemulsion (NA) polymerization. Similar to the TG thermogram investigated by Katsikis et al. [2], there is only one peak at 401.4°C.
for the derivative of the weight loss for pure acrylic latex. While in the case of nanocomposite sample, there are three peaks at 116°C, 197°C and 403.6°C for the derivative of the weight loss. The presented peaks are close to that observed for DTA analysis and are illustrated in the following paragraphs.

The final residual weight percents at high temperatures (600°C) are listed in Table 3. It may be seen that nanosilica can significantly increase residual weight of acrylic latex at high temperatures from 0.6 to 16 percent. The residual weight percent shows that modification of silica particles with oleic acid helps more efficient and stable dispersion. Analogous results have been reported by Ding et al. [12,13]. In the case of nanocomposites, comparing with the initial percentage of nanosilica (5%), we have reached the conclusion that decomposition of the organic components at 600°C is not yet completed and therefore, there is a higher residual weight of nanosilica. This probably is due to the formation of interpenetrating network between the organic and silica components [32].

DTA Curves show that the decomposition temperature ($T_d$) for nanocomposites (containing 5% weight of nano-$SiO_2$) being 405°C is higher than that of pure acrylic latex (397°C). This might be due to the fact that during the degradation process, nanosilica particles may act as thermal insulators and physically protect the remaining polymer from the heat. This causes the volatilization of polymer fragments generated by the pyrolysis to slow down which leads to the enhancement of thermal degradation temperature.

Comparing the TG/DTG curves and DTA peaks for both systems, one can determine that degradation process (exothermic peaks) which goes along with the weight reduction, started just after the thermal decomposition. Other DTA peaks in the temperature region lower than 200°C correspond to the melting and decomposition of non-ionic emulsifier (nonylphenol polyethylene glycol ether) and cetyl alcohol used in the preparation of nanocomposites as well as the water absorbed at the surface of the samples. Note that even if we dried the samples before TG analysis, there would be still some surface moisture on the samples [15]. Furthermore, comparing with the neat latex, this early thermal degradation stage besides emulsifier and hydrophobe and surface moisture, is due to the fact that surface hydroxyl groups of nanomineral oxide particles can partially catalyze the polyacrylate decomposition at the early stage [33-35].

### Particle Size Distribution

Figure 7 presents particle size distribution of colloidal silica resulted from Zetasizer analysis. In the case of waterborne resin based on latex, the particle size distribution plays an important role in the rheology and film formation of latex as well as optical and mechanical properties of the product. To investigate the effect of nanosilica on the thermophysical properties of resins, it is better to reduce the effects of other parameters like particle size distribution. Therefore, in order to make comparison between two systems more effectively, the same average particle size was used for all samples.
size has been designed. Figure 8 shows that the particle size distribution of pure acrylic and nanocomposite lattices are narrow and have similar average size of 125 nanometers.

It is important to note that different processes of miniemulsion polymerization with a considerable quantity of non-ionic emulsifier and co-stabilizers have been used for the preparation of nanocomposite. The miniemulsion process resulted in smaller particle size of nanocomposites compared with the other process as well illustrated by Percy et al. [5,21]. Therefore, in spite of the silica incorporation into the polymeric particles, the diameter enlargement is not evident. Ding et al. [12] has reported similar particle size for the sample with the same silica content.

Hardness

The pendulum hardness test is based on the principle that the amplitude of the pendulum's oscillation will decrease more quickly when supported on a softer surface. The Konig measures time between 6° to 3°.

The results in Table 3 show that nanocomposite (NA) has a superior hardness compared to neat acrylic latex film. Mizutani et al. [4] have reported similar trend for the pencil hardness of nanocomposites and neat samples. Moreover, they correlate the higher hardness to the higher T_g of related latexes.

CONCLUSION

In this study, high solid content nanocomposites of silica/acylate polymer have been prepared by miniemulsion polymerization in semi-continuous operation. Different techniques for the characterization of the nanoparticles show that silica nanoparticles are well located in the polymeric structure of latex. The microscopic images confirm the nanocomposite structure where the nanoparticles of silica are coated with the nanolayers of polymer. This successful procedure is performed via surface modification of silica nanoparticles and an optimized recipe of semi-batch emulsion polymerization. The produced nanocomposites with the solid content of about 42% containing 5% by weight of grafted silica (with respect to polymer) can be used as a waterborne resin in thermally high resistant paints. In this way, the nanocomposite resin is compared with the pure latex with the same monomer structure.

In DTA analysis, the nanocomposites based on silica show an increase of about 8°C in the degradation temperature compared to neat polymer.

DSC Analysis showed that the glass transition temperature of the nanocomposite is higher than that of the pure acrylic latex. This can be attributed to the incorporation of nanosilica with polymer molecules which finally leads to the suppression of molecular movement of the polyacrylate.

The comparison of the nanocomposite resin with pure acrylic resin indicates improved hardness for the nanocomposite.

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