

## Fabrication of Pre-Exfoliated Clay Masterbatch via Exfoliation-Adsorption of Polystyrene Nanobeads

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**Abstract:** The approach studied in the present work produced an exfoliated state of clay layers via confinement of the charged nano-sized polystyrene (PS) beads within the gallery of swollen pristine clay. It was demonstrated that adsorption of the polymer nanobeads dramatically promotes expansion of the clay gallery. A comparative study of incorporation was conducted by employing organo-modified clay along with two different colloid polymer systems: electrostatically stabilized PS nanobeads and cationic monomer-grafted PS nanobeads. The mechanism of adsorption of the monomer-grafted polymer beads onto clay via cationic exchange between the alkyl ammonium group of the polymer nanobeads and the interlayer sodium cation of the layered silicate was verified by using several techniques. As distinct from the polymer nanobeads formed using conventional miniemulsion polymerization method, competitive adsorption of stabilizing surfactant molecules was prevented by grafting the surface functional groups into the polymer chain, thereby supporting the observed effective adsorption of the polymer beads. The presence of surface functional groups that support the establishment of strong polymer-clay interactions was suggested to improve the compatibility of the clay with the polymer matrix and eventually play a crucial role in the performance of the final nanocomposites.

**Keywords:** charged polymer nanobeads, sodium clay, incorporation, cation exchange, surface functional groups.

### Introduction

Polymer-clay nanocomposites (PCN), as their name suggests, are organic/inorganic hybrid materials containing clay sheets of a few nanometers thick and several hundred nanometers long with unique properties when compared to neat polymer and conventional polymer composites.

Up to now, it is believed that due to high aspect ratio and enormous surface area of clay, when highly dispersed in the polymer, clay particles imparts unique combinations of physical and chemical properties that make these nanocomposites attractive for a variety of industrial applications. In order to fully realize the benefits of a polymer/clay nanocomposite, it is necessary that the clay particles become fully exfoliated (delaminated) and uniformly dispersed in the polymer matrix.<sup>1-5</sup> That is why the key issue in preparing PCNs is the achievement of the clay dispersion at both, nano-scale (exfoliation or intercalation) and meso-scale.<sup>1,3,5</sup> The degree of dissociation of the clay layers and their distribution in a polymer matrix is determined by the thermodynamic interactions of the clay layer, the cation residing between the clay layers, and the matrix polymer. One reason for the difficulty

in achieving and maintaining exfoliation and uniform dispersion is the incompatibility between the silicate particle surfaces (which are hydrophilic) and the polymer matrix (which is hydrophobic). Suitable clays to provide compatibility to the organic polymer include chemically modified organophilic cation-exchanged clay. However, fabrication of nanocomposite by melt intercalation of polymer into the organophilic clay has problems due to thermal instability of organic materials modifying inner layer surface of clay. The interaction between onium ion and silicate layer of clay is not thermally stable enough to resist high melt processing temperature of polymer.<sup>3,5-8</sup> The decrease in interlayer spacing that is attributed to the degradation and desorption of organic materials in the gallery at high temperature, hinders the intercalation of polymer into the clay.

The strategy of *exfoliation-adsorption* is to achieve exfoliation of the layered silicate into single layers using a solvent in which the polymer is soluble. It is well known that swollen layered silicates such as montmorillonite can be easily dispersed in an adequate solvent. The polymer then adsorbs onto the delaminated sheets and when the solvent is removed the sheets reassemble, forming an intercalated multilayer structure. The entropy gained by desorption of solvent molecules allows polymer chains to diffuse between the clay layers,

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thereby compensating for decreased conformational entropy.<sup>9,10</sup> Exfoliation-adsorption method is mainly applied to synthesize PCNs with water-soluble polymers, such as poly(vinyl alcohol),<sup>11</sup> poly(ethylene oxide),<sup>11-15</sup> etc.<sup>12</sup> However, it does not lead to high polymer adsorption as the enthalpy change of the process is commonly very small even when surface modification processes to improve interactions between clay and polymers are applied.<sup>7,16</sup> Furthermore, the technique is not applicable to PCNs with hydrophobic polymers such as polystyrene<sup>7,17</sup> and poly(methyl methacrylate)<sup>7,18</sup> due to the lack of compatibility.

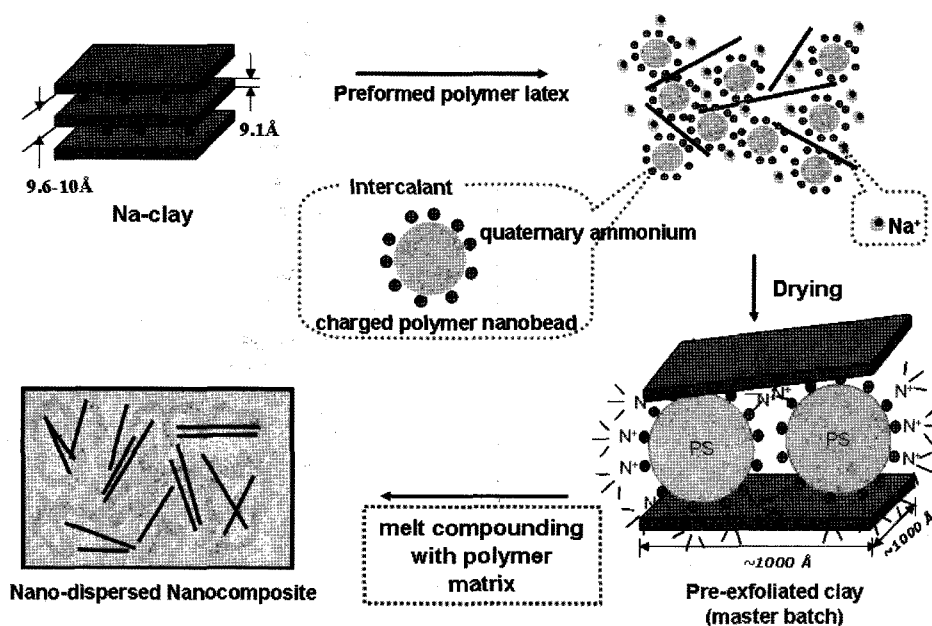
The adjusting the interaction enthalpy between hydrophobic polymer and hydrophilic clay surface can be achieved with assistance of compatibilizers.<sup>1-5,7,19,20</sup> The silicate surface is usually rendered hydrophobic through ion exchange of the sodium interlayer cation with a cationic part (as a rule, onium ion) of an organomodifier. Such compatibilization is believed to be a requisite to achieve desired homogeneous dispersion of clay platelets into the polymer matrix material. Recently, a novel approach, based on exfoliation-adsorption, to prepare PS-clay and PMMA-clay nanocomposites by using unmodified clay and directly surfactant-micellized polymer/toluene has been introduced.<sup>18</sup> It has been shown that pristine clay instead of organo-modified clay can be used and the chemical structure of the polymer can be easily varied. Indeed, the molecular weight or chemical structure of the polymer can be easily controlled simply by changing the starting polymer. However, the interlayer spacing ( $d_{001}$ ) of the intercalated clay not more than about 4 nm was achieved by this method so far.

An alternative route providing facile incorporation of polymer is an ionic exchange between a nanoparticle and an

electrostatically stabilized polymer emulsion. Brittain and co-workers<sup>21</sup> demonstrated an approach to produce exfoliated PMMA nanocomposites in which an aqueous dispersion of pristine sodium montmorillonite was added in a post-polymerization step. Vaia and colleagues also reported that the ionic exchange between electrostatically stabilized PMMA latex and aqueous dispersion of nanoparticles, including layered silicates, provides efficient nano- and molecular scale dispersions of the nanoparticles.<sup>22</sup> Unfortunately, these studies lack for any details related to intercalation of the electrostatically stabilized polymer colloid into clay gallery.

To overcome the issues mentioned above, a novel approach enabling generalization of the PCN synthetic routes is proposed in present study. It is based on the melt intercalation method in conjunction with exfoliation-adsorption via emulsion polymerization. In particular, it is suggested, that highly exfoliated state of clay layers can be achieved through confinement of the preformed charged polystyrene nanobeads within the gallery of swollen Na<sup>+</sup>-montmorillonite. Thus obtained master batch which contains nanoclay in partially dispersed form should be used for preparation of diverse polymer-clay nanohybrids by further melt compounding with additional polymer matrix, as schematically illustrated on Figure 1.

In the present work incorporation of hydrophobic polystyrene beads with diameter of few tens nanometers size into interlamellar space of swollen pristine sodium montmorillonite was aimed to achieve desired dispersion of clay sheets together with required compatibility of the components. To provide understanding of the incorporation mechanism, a comparative study together with organo-modified



**Figure 1.** Schematic diagram of clay exfoliation via incorporation of the PS nanobeads into pristine montmorillonite.

clay was carried out since the intercalation of organic alkyl ammonium salt into layered silicates had been well studied.

## Experimental

**Materials.** The sodium-montmorillonite clay ( $\text{Na}^+$ -MMT) with cation exchange capacity (CEC) of 92.6 meq/100 g ( $9.26 \times 10^{-4}$  mol/g) was supplied by Southern Clay Products Inc. The clay was dried in oven at 80 °C for 24 hrs before use. Dodecyl trimethyl ammonium bromide (DTAB) (molecular formula:  $\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3\text{Br}$ ; FW 308.35) was used as received from Aldrich-Sigma. Styrene and 2,2-azobisisobutyronitrile (AIBN), obtained from Aldrich-Sigma, were purified by conventional method before use. (2,2'-azobis(2-methylpropionamide) dihydrochloride (V-50) as a water-soluble 50/50 wt% water-acetone mixture, potassium persulfate (KPS) of pure grade and Dowex Monodisperse (OH) anion exchange resin from Aldrich-Sigma were used as received. Hydrochloric acid volumetric standard, 0.1 N solution in water purchased from Aldrich was used as received. Cationic monomers [2-(methacryloyloxy) ethyl] trimethylammonium chloride (hereinafter MATMAC) in the form of 75 wt% solution in water and (ar-vinylbenzyl)trimethylammonium chloride (hereinafter VBTMAC) were used as received from Aldrich. Poly(ethylene glycol) (MW 400) purchased from Yakuri Pure Chemicals was used without further purification.

**Organomodification of Clay.** While pristine  $\text{Na}^+$ -montmorillonite was used in this study, the organo-modified clay was introduced for mechanistic study to provide complementary understanding of the exfoliation-adsorption process investigated here, since the mechanism of adsorption of an organic alkyl ammonium salt into layered silicates has been well studied. For this purpose, the intercalant used was dodecyl trimethyl ammonium bromide (DTAB), just the same as the emulsifier employed for emulsion polymerization of polymer nanobeads.

The organoclay samples were prepared from (1% wt) sodium montmorillonite aqueous suspension by the addition of stoichiometric amount (on the basis of CEC of  $\text{Na}^+$ -MMT) of dodecyl trimethyl ammonium bromide solution. The DTAB-clay suspension was stirred with magnetic bar at 250 rpm and 25 °C for 24 hrs and subsequently centrifuged at 16,000 rpm for 20 min to obtain the coagulated matter by removing the supernatant solution. Then, the organoclay (hereinafter: DTAB-clay) was washed several times with de-ionized water until negative reaction with  $\text{AgNO}_3$ , freeze-dried in EYELA FD-1000 freeze dryer and collected for characterization.

### Synthesis of Surface-Charged Polystyrene Nanobeads.

Two different routes have been employed to synthesize cationic polymer nanobeads. According to the first one, the electrostatically stabilized polystyrene (PS) nanobeads (hereinafter: DTAB) were synthesized via conventional micro-

emulsion polymerization using cationic surfactant DTAB and organic phase initiator AIBN. The routine procedure is widely employed and well described elsewhere.<sup>23</sup> For application in this study, the procedure was newly developed to adjust several parameters such as the polymer particle (hereinafter: nanobead) size along with size distribution, electrostatic stability, surface charge, etc. Free-radical emulsion polymerization of styrene monomer was carried out in a three-necked round bottom flask fitted with a mechanical stirrer and equipped with a water bath and a nitrogen gas supply system. The surfactant was added to 220 g of de-ionized water to yield 1.0 wt% emulsion. The medium adjusted to pH = 14 by 1 N NaOH, was vigorously stirred at 400 rpm under nitrogen atmosphere and subsequently heated to  $70 \pm 1$  °C. An hour later, a mixture of St [20 g] and AIBN, preliminary stirred in a beaker, was added to the reactor. 15 min later, 10 g of 2 wt% aqueous solution of KPS was injected into the reactor using a glass syringe. Polymerization reaction was quenched after 6 hrs.

The obtained latex containing polymer nanobeads was cleaned by dialysis against de-ionized water until the conductivity of the surrounding water reached a constant value. Such rigorous cleaning procedure was essential to avoid undesirable competitive adsorption of free surfactant molecules onto clay surface.

Another two types of polymer nanobeads were prepared via emulsifier-free emulsion polymerization:

1) PEO-stabilized PS nanoparticles (hereinafter: MAT nanobeads) were synthesized by ternary copolymerization with the cationic monomer MATMAC as a second comonomer. The recipe and experimental conditions were assigned on the basis of the results described in the literature.<sup>24</sup> To synthesize monodisperse cationic polymer nanobeads in nanosize range (at least less than 100 nm) the recipe was designated as follows: St [37.49 g], PEO/St [1/90 (mol)], MATMAC/St [5/90 (mol)], V50 [(0.1 mol/l) 10 mL], water 430 g.

The designated amount of all reactants, except the initiator, was initially mixed with water under agitation at 400 rpm at room temperature, and the mixture was extensively purged with dry nitrogen gas for about 45 min, whereupon the temperature was raised to  $70 \pm 1$  °C. About 5 min later, initiator aqueous solution was injected into the reactor using a glass syringe. The polymerization was terminated after 6 hrs.

2) Another trial to synthesize suitable nanoparticles (hereinafter: VBT nanobeads) was made via two-step seeded emulsifier-free emulsion polymerization. By the use of highly surface-active, functional comonomers in two-stage emulsion polymerization it is possible to independently control both particle size and amount of surface group (or charge) concentration.<sup>23</sup> Purified latex obtained in the first stage with a minimal amount of MATMAC was used as a seed. At the second stage of emulsion polymerization VBTMAC comonomer and additional amount of the principal monomer, e.g. styrene, were added to ensure bonding of the functional

monomer to the particle surface. The ingredients were emulsified by stirring at a rate of 280 rpm under N<sub>2</sub> atmosphere and allowed to equilibrate at ambient temperature for several hours until swelling of the latex particle by the monomer was complete. Then, initiator aqueous solution was injected into the reactor using a glass syringe, and the polymerization was terminated after 6 hrs.

Prior to characterization, the colloidal particles were cleaned by dialysis against deionized water until the conductivity of the surrounding water reached a constant value (i.e., close to the conductivity of deionized water). The dialysed latexes were further purified by two centrifugation-redispersion cycles to separate water-soluble polyelectrolytes from the colloidal particles.

#### **Incorporation of the Polymer Nanobeads into Clay.**

1.0 wt% aqueous suspension of sodium montmorillonite was stirred to allow swelling of clay particles into individual platelets whereupon it was mixed with an equivalent amount of colloidal polystyrene (PS) nanobeads to produce the PS-incorporated clay. In order to suppress undesired aggregation of the polymer nanobeads, the stoichiometric quantity of the PS nanobeads which was calculated on the basis of basal surface area<sup>25</sup> of clay sheet was added. The heterocoagulated matter was centrifuged at 20,000 rpm to extract the precipitate from the suspension. The repeated washing procedure was carried out until the conductivity of the supernatant reached a constant value close to the conductivity of deionized water. The obtained sediment was subsequently freeze-dried in EYELA FD-1000.

**Characterization.** The size and morphology of nanobeads were characterized by means of both dynamic light scattering (DLS) employing electrophoretic light scattering spectrophotometer (ELS-8000, Photal Otsuka Electronics) and transmission electron microscopy (TEM, Philips CM 30, at acceleration voltage of 200 kV).

Zeta potential derived from electrophoretic mobility of colloidal nanobeads was measured using electrophoretic light scattering (ELS) technique (ELS-8000, Photal Otsuka Electronics), whereas colloidal potentiometric titration technique was applied to estimate the surface charge density of the obtained nanobeads. Prior to titration, synthesized polymer nanobeads were separated from coagulum by filtering and further cleaned by dialysis and ion-exchange on anionic exchange resin. Cationic groups at surface of the nanobeads were titrated with hydrochloric acid after ion exchange to -OH form. Potentiometric titration was performed with TitraLab 860 (Potentiometric Titration Workstation, Radiometer Analytical) using inflection point (IP) method and multi-combined electrode.

Characterization of the surface functionality of the polymer nanobeads was performed with TOF-SIMS and XPS surface analyses. The TOF-SIMS spectra were acquired by using a model PHI 7200 TOF-SIMS/SALI instrument of Physical Electronics. Negative ion spectra were used to quantify N in

the surface layers after sputtering the outer layers. XPS analysis was carried out on the X-ray photoelectron spectroscope SSI, 2803-s with monochromatic Al K $\alpha$  X-rays (1,486.6 eV) operated at 100 W and 15 kV in a chamber pre-sure of approximately  $2.0 \times 10^{-9}$  Torr. The electron takeoff angle was 45° with respect to the sample surface. The XPS data from the regions related to the C (1s), Al (2p), Si (2p), Na (1s), and N (1s) core levels were recorded for each sample. The binding energy scales were adjusted to the highest C (1s) peak position equal to 284.6 eV.

Morphological observation of the polymer-incorporated clay at nanometer scale was performed using transmission electron microscopy (TEM, Phillips CM 30), at accelerating voltage of 200 kV. A portion of the PS nanobeads-clay suspension was casted on a carbon-coated grid and imaged without staining.

Dispersion of silicate layers was evaluated by means of wide angle X-ray diffraction (WAXD) using MXP18A-HF, MacScience diffractometer. Cu K $\alpha$  ( $\lambda = 1.56 \text{ \AA}$ ) was used as an X-ray source at a generator voltage of 40 kV and current of 100 mA. The  $2\theta$  scanning rate was 0.1 degree/min in the range of  $2\theta = 2\text{--}10^\circ$ .

Morphology of polymer nanobeads adsorbed to silicate surface was observed using field emission-scanning electron microscopy (FEI XL-30 FEG FE-SEM) at accelerating voltage of 8 kV. Au/Pt coating was applied onto the specimen, which was deposited onto a carbon film.

## **Results and Discussion**

#### **Electrostatically Stabilized PS Nanobeads (DTAB).**

Microemulsion polymerization with use of cationic surfactant DTAB and organic phase initiator AIBN allowed produce positively charged (DTAB in Table I), monodisperse polystyrene nanobeads (Figure 2(a)). It was presumed that, with a hydrophobic polymer and a low concentration of functional groups, all of the titratable groups are on the surface of the particles. Any buried groups would not have been ion-exchanged, and would therefore have no corresponding OH<sup>-</sup> counterion upon ion exchange on anionic exchange resin. Since there is only one titratable counterion for each surface fixed group, the titration equivalence point provides an accurate count of the number of fixed groups on the nanobead

**Table I. Characteristics of the Polymer Colloid Nanobeads**

Characteristics	Method	DTAB	MAT	VBT
$d_n$ , nm	DLS	40	77	96
Zeta potential, mV	ELS	+32	+46.8	+63.6
N, at%	XPS	1.03	1.07	1.31
N, a.u.	SIMS	-	26	33
$\sigma_0$ , $\mu\text{C} \cdot \text{cm}^{-2}$	Titration	2	81	162

surface, from which it is easy to calculate the surface charge density<sup>26,27</sup> ( $\sigma_0$ , Table I).

**Monomer-Grafted PS Nanobeads (MAT, VBT).** Stable monodisperse MAT nanobeads have been obtained using MATMAC as can be implied from TEM image (Figure 2(b)) and high zeta potential value (Table I). Incorporation of the cationic monomer into the copolymer chain of the nanobeads was confirmed from the chemical composition via surface analysis (TOF-SIMS and XPS) and surface charge density (Table I), which also serves as indicator of the functional groups presenting at the surface. MAT nanobeads possess more than 40 times higher surface charge density against the PS nanobeads synthesized by conventional emulsion polymerization. Introduction of the second surface-active comonomer VBTMAC into polymer chain of the MAT seed allowed control independently both particle size (still non-exceeding 100 nm) and surface group concentration. As a result, the nanobeads with dramatically increased surface charge density due to higher comonomer content at the surface were obtained. Indeed, surface charge density of VBT nanobeads is a double value of that of MAT nanobeads (Table I). This is also in good compliance with results of surface analysis performed with XPS and ToF-SIMS.

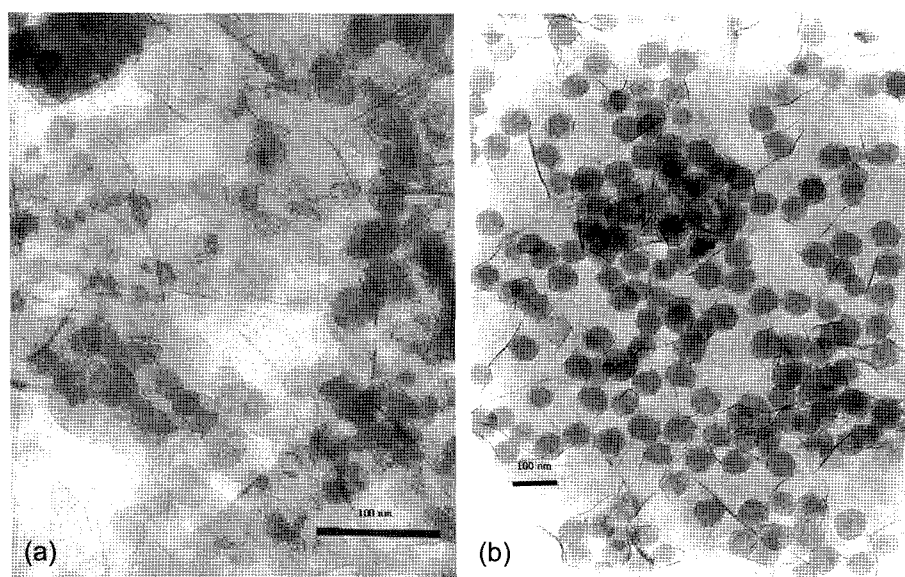
**Incorporation of the Polymer Nanobeads into Clay.** Transmission electron micrographs (Figure 2) visualized a random arrangement of the monodisperse polystyrene nanobeads confined between sparsely dispersed clay platelets. The obtained morphology allows implying that the mutual arrangement of the two phases owes to the sandwiching of the polymer beads between the exfoliated clay sheets upon heterocoagulation. It is worth to note that such a dispersed state is maintained after complete removal of solvent upon drying,

implying that the polymer beads confined between clay sheets prevent the silicate layers from restacking. Obviously, it is caused by presence of certain polymer-clay interactions, as well as relaxation of the van der Waals forces, which originally retain silicate layers together in the lattice of pristine clay. However, along with fully delaminated single clay layers, partially stacked clay tactoids each comprised by a few silicate sheets, can be readily observed, particularly in case of electrostatically stabilized DTAB nanobeads (Figure 2(a)). Incomplete exfoliation of clay nanoplatelets could be caused by limited swelling of clay as well as nonswelling impurities of clay. It can be implied from the TEM observation that a homogeneous agglomeration of the DTAB nanobeads also presents. It is attributed to a competitive adsorption of surfactant molecules which are not covalently bonded with polymer alkyl chain. It indicates on necessity of grafting of a surface-active monomer into polymer chain.

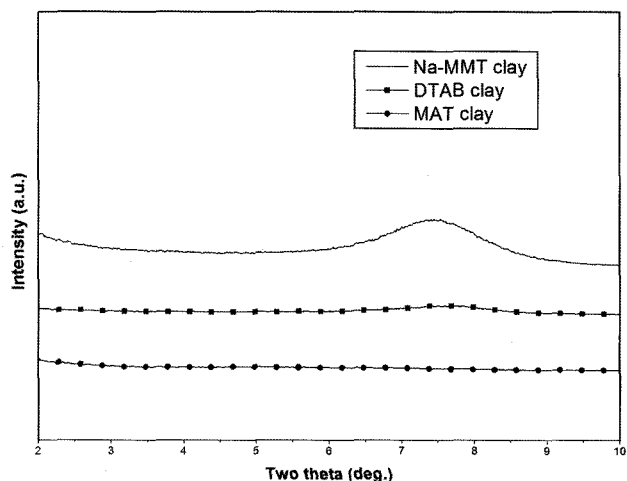
The increased electrostatic stability of cationic monomer-grafted MAT nanobeads as compared to DTAB nanobeads (Figure 2(b)) is in good agreement with its higher zeta potential value and surface charge density confirmed by chemical analysis (Table I).

The incorporation of PS nanobeads into clay gallery can be deduced from the WAXD patterns (Figure 3). The layered structure of the native clay suffered disordering expansion induced by incorporation of PS nanobeads. It results in disappearance of the structural ordering peculiar to pristine clay. Thus, it can be implied that dramatic expansion of clay gallery owes to the incorporation of the polymer nanobeads within the silicate layered structure.

To ascertain mechanism of adsorption of the PS nanobeads into clay gallery, atomic composition and chemical state at



**Figure 2.** Bright field TEM micrographs of the (a) surfactant-stabilized PS nanobeads (DTAB) and (b) monomer-grafted PS nanobeads (MAT) incorporated into pristine sodium montmorillonite clay, taken at magnification  $\times 60,000$  (bar denotes 100 nm across and upright).



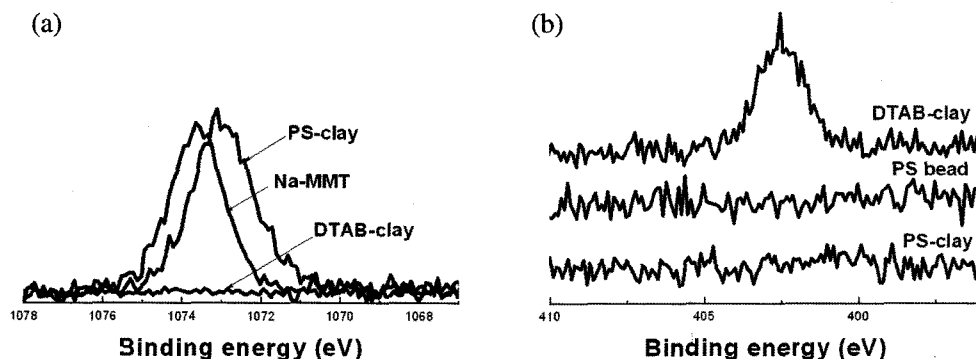
**Figure 3.** Wide angle X-ray diffraction patterns of pristine clay and clay pre-exfoliated by interlamellar incorporation of surfactant-stabilized polymer nanobeads (DTAB); monomer-grafted polymer nanobeads (MAT).

the surface including clay-polymer interface were determined with X-ray photoelectron spectroscopy (XPS). Due to the unique ability of XPS to determine quantitatively the local bonding with high depth resolution (at least in the outer 10 nm of materials),<sup>28</sup> it was suggested to study the chemical nature of the adsorbed species at the surface including polymer-clay interface. The surface analysis was performed on clay incorporated with the PS nanobeads along with the two references: pristine sodium-montmorillonite and organo-clay (DTAB-clay).

Comparison of the photoelectron spectra reveals disappearance of Na (1s) peak (Figure 4(a)) together with pronounced N (1s) peak in case of the organo-clay (Figure 4(b)). This suggests that the interlayer sodium ions of clay are almost fully replaced by the onium ions of the DTAB molecules in the organo-modified clay. Whereas only slightly decreased intensity of sodium peak can be noticed in case of

the clay incorporated with DTAB nanobeads. The observed shift in binding energy of sodium ion in DTAB-incorporated clay with respect to pristine clay can be ascribed to establishment of certain interaction between sodium ions of clay and polymer.<sup>29,30</sup> For further quantitative estimation, photo-emission peak areas were determined by Gaussian-Lorentzian fitting functions and corrected for atomic sensitivity factors. The atomic abundances of the elements were determined from peak width of the photoelectron, and the averages of the two parallel repetitions were calculated (Table I).

The moiety of the ion-exchanged sites of clay (i.e. sodium ions) was estimated as a difference between the normalized values of the experimentally obtained abundance of the Na ions in pristine clay and the ions remained un-removed upon the adsorption of the PS nanobeads (Table II). The normalization was done taking into account the atomic composition of the unit cell of clay,<sup>25,31</sup> with respect to Al and to Si, correspondingly (viz. 3.33 for Al and 8 for Si), because it was suggested that no chemical state change of these elements had taken place during the ion exchange processes.<sup>29,30</sup> From thus normalized moieties of sodium ion it is clear that a major quantity of the sodium ions (about 84%) has been replaced by the onium ions in the organomodified clay, whereas only merely 1.3% in the DTAB nanobead-incorporated clay. In fact, the latter number is in the error limits of the employed analytic technique. An attempt to increase the amount of functional groups at the bead surface by increasing the surfactant content (not presented here) does not alter the number of exchanged sites. This important finding indicates on the necessity of grafting of the functional groups into the polymer chain to provide stronger polymer-clay interactions through the cationic exchange. On the other hand, the amount of Na ions exchanged upon adsorption of MAT nanobeads, is about five times higher as compared to the former system (Table II). Furthermore, near one fourth of Na ions was involved in cationic exchange with ammonium ions of VBT nanobeads (Table II). Thus, the increase in abundance of surface groups not only enhances overall col-



**Figure 4.** (a) Na (1s) and (b) N (1s) spectra of the pristine clay (Na-MMT clay), the organoclay (DTAB-clay) and the clay heterocoagulated with PS nanobeads (DTAB).

**Table II. Atomic Abundances of Na and the Normalized Moiety of the Ion-Exchanged Sites per Unit Cell of Clay Estimated from XPS Data**

Atomic Abundance	Na-MMT	Organo-Clay	DTAB-Clay	MAT-Clay	VBT-Clay
Na	2.13	0.28	1.21	1.95	1.56
Al	8.69	7.28	5.04	8.75	9.08
Si	22.29	17.88	12.74	20.95	20.01
Na <sup>(Al)</sup> <sup>a</sup>	0.82	0.13	0.80	0.74	0.57
Na <sup>(Si)</sup> <sup>b</sup>	0.76	0.13	0.76	0.74	0.62
Na <sup>avg</sup> <sup>c</sup>	0.79	0.13	0.78	0.74	0.60
Exchanged sites <sup>d</sup>	--	0.66	0.01	0.05	0.19

<sup>a</sup>Atomic abundance of Na normalized with respect to Al, per unit cell of clay. <sup>b</sup>Atomic abundance of Na normalized with respect to Si, per unit cell of clay. <sup>c</sup>Averaged abundance of Na calculated from <sup>a</sup> and <sup>b</sup>. <sup>d</sup>Estimated as a difference between the normalized values of the abundance of the Na ions in pristine clay and the ions remained un-removed upon the adsorption of the PS nanobeads; the determined average moiety of the ion exchangeable sites in Na-MMT is 0.79 ca. per unit cell of clay.

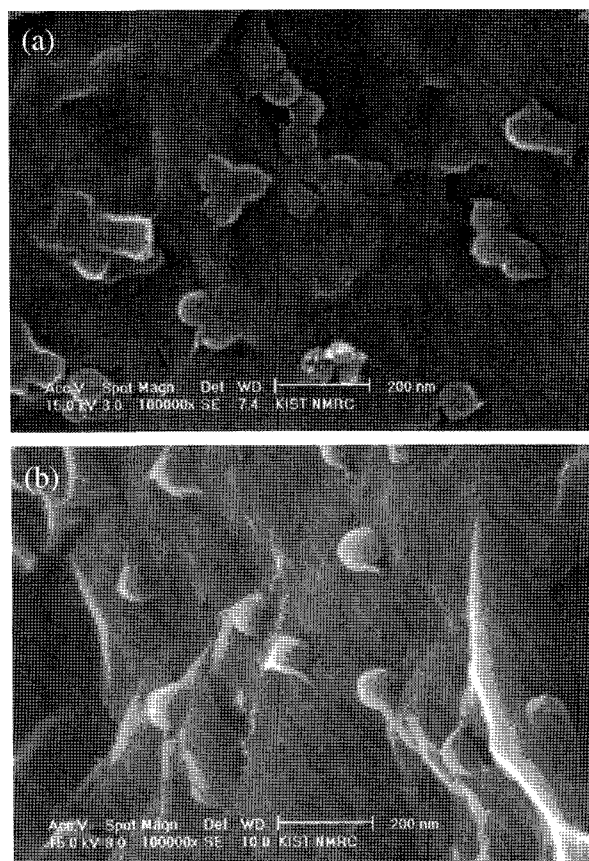
loidal stability of the nanobeads, but definitely promotes cationic exchange and, consequently, the adsorption of nanobeads onto silicate surface. Introduction of the second surface-active comonomer with quaternary ammonium groups (VBTMAC) resulted in the formation of stable nanobeads with higher surface charge (Table I) and, consequently, in random adsorption of the nanobeads on clay surface that is distinct from that of the MAT nanobeads on FE-SEM images as shown in Figure 5(a). Indeed, interlinking a few of MAT nanobeads (in Figure 4) when attached to silicate surface can be ascribed to a slight aggregation of them. On the other hand, observation of randomly adsorbed individual VBT nanobeads (Figure 5(b)) serves as an augmenting confirmation of enhanced electrostatic stability of the colloidal nanobeads due to increased surface functionality of the latter as it was discussed above.

## Summary

It has been shown that the hydrophobic charged polymer nanobeads can be successfully incorporated into gallery of unmodified sodium montmorillonite. The polymer beads confined between clay sheets are able to prevent silicate layers from restacking and further, maintain the exfoliated state of clay. Mechanism of nanoconfinement of the different surface charged polymer nanobeads into clay gallery through careful analysis of surface chemistry has been discussed.

The results of polymer-clay interfacial analysis indicate that it is the cationic exchange that is responsible for the decrease in moiety of sodium ions in the clay exfoliated with the monomer-grafted PS nanobeads (MAT and VBT). Furthermore, the increased abundance of surface groups not only results in enhanced stability of the polymer nanobeads, but also promotes the cationic exchange, and consequently, improves compatibility of clay with polymer matrix.

As distinct from the incorporation of polymer nanobeads



**Figure 5.** FE-SEM images of monomer-grafted polymer nanobeads: (a) MAT and (b) VBT, randomly adsorbed onto clay surface.

(DTAB) synthesized by conventional miniemulsion polymerization method, by grafting of the surface functional groups into the polymer chain, competitive adsorption of stabilizing surfactant molecules can be prevented, allowing the observed effective adsorption of the polymer nanobeads

onto silicate surface through the ion exchange of intergallery cation of clay for onium ion presenting at the surface of polymer nanobead.

## Conclusions

The approach, studied in the present work, involves loading the clay gallery with preformed polymer nanobeads bearing a cationic functional group on its surface. It has been demonstrated that adsorption of the polymer nanobeads dramatically promotes expansion of clay gallery with maintaining the exfoliated structure of the latter upon complete drying.

The mechanistic examination presented serves as a strong evidence for adsorption of the polymer beads onto clay via cationic exchange. As distinct from the polymer nanobeads formed using conventional miniemulsion polymerization method, by grafting of the surface functional groups into the polymer chain, competitive adsorption of stabilizing surfactant molecules can be prevented, allowing the observed effective adsorption of the polymer beads.

It has been suggested that the presence of strong polymer-clay interactions will improve compatibility of clay with polymer matrix. The latter eventually is believed to play a crucial role in desired improvement of mechanical performance of the nanocomposites that should be prepared by letting down of the pre-exfoliated masterbatch with polymer matrix.

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