

Mechanistic examination of pre-exfoliating confinement of surface-functionalized nanobeads within layered silicates

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Introduction

Many properties of polymer-layered silicate nanocomposites are a function of the extent of dispersion of the individual clay platelets into a continuous polymer matrix as well as of the compatibility of the two intrinsically non-miscible materials [1-6].

To overcome the drawbacks in preparation of layered silicate nanocomposites found to date, an alternative technique, based on exfoliation-adsorption, to directly use unmodified layered silicate and colloid polymer particles of few nanometer size has been proposed in the current work. The approach involves loading the gallery of layered silicate with preformed polymer nanobeads bearing a cationic functional group on its surface. In this way it is expected that desired strong interactions between host clay surface and guest polymer particles will be provided due to cationic exchange of interlayer sodium ions for ammonium cations at the surface of polymer beads. Furthermore, it is suggested that adsorption of polymer nanobeads through cationic exchange of inter-gallery cation of clay for onium ion at the surface of polymer nanobead not only improves compatibility of clay with polymer matrix, but, what is essential, dramatically promotes expansion of clay gallery.

Experimental

Synthesis of charged polymer nanobeads. Ultrafine charged polymer nanobeads based on poly(ethylene oxide) (PEO) macromonomer and polystyrene (PS) have been synthesized by ternary copolymerization with cationic monomer (2-(methacryloyloxy)ethyl) trimethylammonium chloride (MAT) as a second comonomer via emulsifier-free emulsion polymerization.

To increase surface charge of the polymer beads and thereby, enhance its stability, seed emulsion polymerization with other cationic monomer vinyl benzyl trimethyl ammonium chloride (VBT) was also employed independently.

The size of fine nanoparticles was characterized using both dynamic light scattering (DLS) and transmission electron microscopy (TEM) whereas colloidal titration techniques were applied to estimate the surface charge density of the obtained particles.

Incorporation of the polymer nanobeads into layered silicates. Prior to incorporation into layered silicate, the obtained polymer nanobeads were purified by dialysis against deionized water until the conductivity of the surrounding water reached a constant value. 1.0 wt % aqueous suspension of sodium montmorillonite was allowed to swell into individual platelets whereupon it was mixed with an equivalent amount of polystyrene latex to suppress undesired aggregation of the polymer beads. The quantity of the polymer latex was calculated on the basis of basal surface area [7] of silicate sheet. Microstructure of polymer-incorporated layered silicate was analyzed by using XRD and TEM.

Mechanism of incorporation was studied employing XPS, ToF-SIMS etc. The atomic abundances of the elements were calculated from area intensities of the photoelectron. For all clay samples, the atomic abundances of Na were obtained as a ratio to Al and Si, because it is apparent that no chemical state change of Al and Si had taken place during the ion exchange processes. The moieties of ion-exchanged sites were further normalized to unit cell of clay.

Results and discussion

The incorporation of polystyrene beads into the gallery of layered silicate can be deduced from the WAXD patterns. The layered structure of the native silicate suffers disordered expansion induced by incorporation of the nanometer-ranged PS beads.

Transmission electron micrographs also visualized a random

arrangement of the monodisperse polymer latex confined between sparsely dispersed clay platelets. Along with fully delaminated single clay layers, partially stacked clay tactoids each comprised by a few silicate sheets, can be readily observed. The obtained morphology allows suggest that the observed mutual arrangement of the two phases owes to the sandwiching of the polymer beads between the exfoliated clay sheets. It is worth to be noted that such dispersed state is maintained after complete vaporization of solvent upon drying. This fact implies that the polymer beads once confined between clay sheets do not escape outward, thereby preventing the silicate layers from restacking. It can serve as strong evidence for firm adsorption of guest polymer beads onto clay, very likely, via cationic exchange mechanism, as it is suggested in present work.

Introduction of the second surface-active comonomer with quaternary ammonium groups (VBT) resulted in the formation of particles with higher surface charge and, consequently, in random adsorption of them on clay surface that is distinct from adsorption of PEO-PS/MAT nanobeads.

To further ascertain the mechanism of the adsorption of the nanobeads into the gallery of layered silicate, surface analysis was performed employing XPS and ToF-SIMS. Experimentally determined average amount of Na in one unit cell of original silicate (0.67) reveals good agreement with unit-cell formula [7], implying that it is clear that actually one third of Na ions were involved in exchange with ammonium ions of PEO-PS/MAT/VBT guest nanobeads. Thus, the increase in abundance of surface groups promotes cationic exchange and, consequently, the adsorption of nanobeads onto silicate surface.

The results of surface analysis performed with ToF-SIMS have been found in good compliance with XPS observations.

Conclusions

The results of quantitative analysis performed with XPS and SIMS along with TEM have proved that cationic exchange is responsible for strong polymer-clay interactions leading to adsorption of the polymer beads onto clay surface. Moreover, the polymer beads thus confined between clay sheets are able to prevent the silicate layers from restacking and further, maintain exfoliated state of clay. It is suggested that the presence of strong polymer-clay interactions will play a crucial role in desired retaining delaminated clay sheets upon melt processing with polymer matrix.

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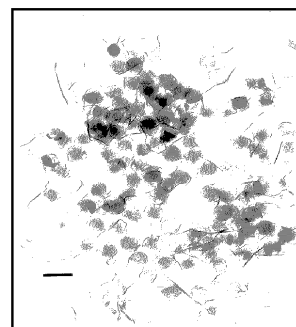


Figure 1. TEM micrograph shows incorporation of polymer nanobeads in-between silicate nanosheets. The solid bar in the micrograph represents 100 nm.