

Spray-Dried Microspheres as a Route to Clay/Polymer Nanocomposites

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ABSTRACT: A new strategy for the preparation of well-dispersed clays in a polymer matrix by a spray-drying method is presented. Scanning electron microscopy and transmission electron microscopy measurements show that the spray-drying process produces clay/polymer microspheres in which the clay is trapped in a well-dispersed state throughout the polymer matrix. The microspheres have been successfully extruded into clay/poly(methyl methacrylate) nanocomposite bulk structures without any perturbation of the well-dispersed clay nanostructure in the original microspheres. Transmission electron micros-

copy and small-angle X-ray scattering show that the clay particles in the extruded materials range from single platelets to simple tactoids composed of a few stacked clay platelets, indicating an excellent degree of dispersion. The results show that sprayed microspheres are very good precursors for further processing such as extrusion or melt blending with other polymers for bulk nanocomposite fabrication. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1550–1556, 2008

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INTRODUCTION

Nanocomposites of a clay dispersed in a polymer matrix have been extensively studied. This has been driven by the fact that clays are abundant in nature and consist of nanometer-sized platelets. Up to now, the favorite method for clay/thermoplastic nanocomposite fabrication has been melt intercalation.¹ Practical economic reasons are at the heart of these developments, which will allow nanocomposite fabrication to be compatible with current industrial mixing and processing techniques such as extrusion and injection molding. However, during the process of producing polymer/clay nanocomposites, clay nanoparticles easily aggregate, and this negates any advantage associated with nanometer dimensions. It is hoped that the clay platelets will intercalate, and possibly exfoliate, with assistance from some significant applied shearing forces and thus disperse uniformly throughout the polymer melt, which is then processed to make a final product. Nanocomposites

can also be prepared by solution intercalation with a solvent in which the polymer is soluble and the clay platelets are swellable.² When the polymer and clay solutions are mixed, the polymer chains enter the clay galleries of the suspended clay particles and cause an increase in the spacing between the platelets. Solvent-derived nanocomposites can often lead to more intimate mixing and delamination than melt-blended materials because of the ability of appropriately chosen solvents to penetrate the layered silicate gallery, encouraging them to come apart and achieve intimate contact with the dissolved polymer. It has been reported that a poly(ethylene oxide)/clay nanocomposite prepared by this method shows better dispersion than that produced by melt extrusion.³ However, the development of the solution intercalation method has made very few commercial gains (other than for thin coatings) on account of the impractical use of large quantities of solvents as well as excessive evaporation time.

Here we present an alternative method to produce polymer/clay nanocomposites by using the technique of spray drying, which has not, to the best of our understanding, been applied to making polymer nanocomposites. Spray drying is a widely used

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method of drying a liquid droplet feed by means of a flow of hot gas or air. This method has successfully been applied to the production of biopolymer microsphere materials for drug delivery applications.^{4,5} In this work, we used the technique to encapsulate (in a very dispersed state on the nanoscale) an organically modified layered silicate, before eventually blending this mixture into a polymer melt. Because the process involves both solution and blending treatments, it can be considered a new process, a hybrid of both methodologies of nanocomposite formation that uses the intimacy of solvent mixing to produce materials that ultimately can be melt-blended while retaining the improved delamination. To fabricate polymer microspheres that encapsulate clay nanoparticles, the chosen polymer and organoclay are first both dispersed within a suitably chosen solvent or solvent mixture. The condition under which the final dispersion must be stable with respect to any precipitation and/or agglomeration over the timescale taken to spray-dry the dispersion must be satisfied. Through the spraying of the solutions of the polymer and clay through hot air, micrometer-sized liquid droplets are formed with a large surface-to-volume ratio, and on account of their small size, they are easily heated in a short time to a temperature at which solvent evaporation is rapid. As the solvent is removed, the polymer and clay that are initially both homogeneously dispersed in the solvent are by necessity also homogeneously mixed with each other in the resultant nanocomposite microspheres, with the clay unable to reorganize and form tactoids or bigger agglomerates during this part of the process. The microspheres of nanocomposite thus reflect to a high degree the original intimate relationship between the nanoclay and polymer in the original, liquid dispersion state. To convert the nanocomposite microspheres to a bulk material, the particles are then melted or fused together by, for example, extrusion. A schematic of the fabrication of polymer/clay nanocomposites by the spray-drying method is shown in Figure 1.

This article reports the fabrication of a poly(methyl methacrylate) (PMMA)/organoclay nanocomposite, showing that the spray-drying method indeed offers a viable alternative route for nanocomposite fabrication. To arrive at these conclusions, nanocomposite microspheres and bulk material resulting from their extrusion were characterized with scanning electron microscopy (SEM), transmission electron microscopy (TEM), and small-angle X-ray scattering (SAXS) measurements.

EXPERIMENTAL

Materials

The polymer PMMA (weight-average molecular weight by gel permeation chromatography $\sim 15,000$)

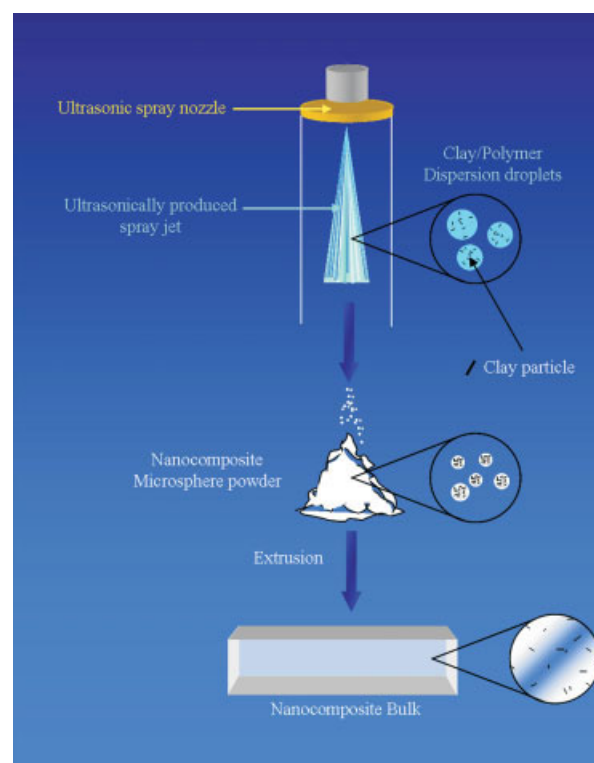


Figure 1 Schematic showing the production of polymer/clay nanocomposite materials by the spray-drying technique. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was purchased from Aldrich (Castle Hill, Australia) (200336-100G). The organoclay used in these studies was Cloisite 30B (Southern Clay Products, Gonzales, TX), which is a natural montmorillonite modified with the ternary ammonium salt methyl tallow bis-2-hydroxyethyl quaternary ammonium. The clay particles were generally 5–10 μm in size (50% < 6 μm) and were composed of agglomerates of clay tactoids. The clay platelets were typically 100–150 nm in diameter and ~ 1 nm thick, and the d_{001} -spacing of the organically modified clay was 18.5 Å.

Dispersion preparation

A 0.5% concentration of PMMA in acetone was made by the direct addition of the polymer to the solvent, which was left for several hours to dissolve. Cloisite 30B does not disperse in acetone, but it was found that Cloisite 30B disperses well in *N,N*-dimethyl acetamide (DMA), with the resultant dispersion also miscible with acetone and showing no instability with respect to precipitation of the organoclay. Therefore, a 1% concentration of Cloisite 30B in DMA was made by the addition of an appropriate weight of organoclay to the solvent and then sonication with a Misonix (Farmingdale, NY) XL-2020 600-W, 20-kHz ultrasonic liquid processor equipped with a 0.5-in.-diameter ultrasonic horn with a tita-

nium tip for several minutes to disperse the clay (setting 5). An appropriate volume of the clay dispersion was added slowly with a pipette to a calculated volume of the PMMA dispersion, with continual sonication of the acetone with the ultrasonic horn (setting 5). The final dispersion was a 0.5% concentration of solids, with the clay content being 2 wt % of the solids.

Spray drying

An Ismatec micropump (Glattbrugg, Switzerland) carried the liquid dispersion through Teflon tubing to a Sonotek (Milton, NY) ultrasonic nozzle (120 kHz) attached to the top of a vertically held heated glass column ($\sim 90 \text{ mm} \times 1000 \text{ mm}$, $100\text{--}125^\circ\text{C}$). The ultrasonic spray nozzle atomized the liquid stream into a jet of micrometer-sized droplets (average diameter $\sim 20 \mu\text{m}$) into a flow of preheated Ar gas exiting from a specially designed shroud around the tip of the ultrasonic nozzle. The spray-dried material was collected with a specifically designed filter system.

Extrusion

The powder was fed into a Haake Minilab microcompounder twin-screw extruder with a corotating screw configuration. The melt was processed for 10 min at a temperature of 200°C with a screw speed of 50 rpm. The melt was then extruded into a holding vessel of a DSM injection molder (Evansville, IN) held at a temperature of 200°C and injected into a mold with an injection pressure of 1.5 bar. The injected piece was in the form of a tensile specimen with a length of 90 mm, a width of 10 mm, and a thickness of 1.5 mm.

SEM

SEM samples of the spray-dried powder were prepared by careful deposition of a small amount of the microsphere powder with a spatula onto the top side of double-sided tape that had been stuck with the other side to a carbon stub. The sample was then coated with a thickness of 50 \AA of carbon *in vacuo* to prevent charging during SEM. This is a standard procedure known not to introduce any visible artifacts into the examination at the magnifications used here. The scanning electron microscope was a JEOL JSM-6400 (Tokyo, Japan) with an attached Noran Instruments Voyager series IV X-ray microanalysis system (Middleton, WI). The scanning electron microscope was operated at an accelerating voltage of 15 kV.

TEM

The spray-dried microsphere powder was set in Buehler's Epo-Thin low viscosity epoxy (Lake Bluff,

IL) by vacuum impregnation to extract unwanted air gaps. The set resin was appropriately trimmed to give a small cross section of $\sim 0.3 \times 0.3 \text{ mm}^2$ before being sectioned by ultramicrotoming with a Leica Ultracut UCT (Vienna, Austria) into sections approximately 50 nm thick and $\sim 0.3 \times 0.5 \text{ mm}^2$ in size with a Diatome Ultra 35° diamond knife (Biel, Switzerland). The sectioning speed was automated and set at 0.3 mm/s for 50-nm cuts. Samples were then collected and dispensed onto a 3-mm, 200-mesh copper-based holey carbon TEM grid with $90\text{-}\mu\text{m}$ grid squares. The extruded samples were also trimmed and microtomed in a similar fashion.

The samples for TEM were investigated with a JEOL 2000FXII transmission electron microscope operating at 100 kV along with an Oxford PentaFET analytical energy dispersive microanalysis (EDS) (High Wycombe, UK) running off the Link ISIS system. Images were obtained with standard bright-field TEM with Digital Micrograph.

SAXS

SAXS was carried out with the SAXSess system with a charged coupling device detector and line collimation from Anton Parr (Graz, Austria). The X-ray source was $\text{Cu K}\alpha$ ($\lambda = 0.1542 \text{ nm}$), and the sample-to-detector distance was 307 mm. Corrections were made for instrumental background. The range of the momentum transfer vector (Q) = $\sin \theta 4\pi/\lambda$ was $0.06\text{--}0.5 \text{ nm}^{-1}$. The desmearing of the scattering curve was performed with the Saxsquant 2.0 program. The beam profile was measured and incorporated into the data evaluation by a desmearing program (Anton Parr, Graz, Austria).

RESULTS AND DISCUSSION

Morphology of the microspheres

Figure 2 shows an SEM image of clay/polymer microspheres produced by the spray-drying method. The microspheres typically have sizes in the range of $5\text{--}10 \mu\text{m}$ and appear to have a relatively smooth surface.

For the TEM analysis, the microspheres were first set in an epoxy resin, and then $\sim 50\text{-nm}$ -thick microtomed slices of this set resin were deposited carefully onto holey carbon-coated copper TEM grids. The dimensions of the clay platelets composing the organoclay used in these studies are typically 120 nm across and $\sim 1 \text{ nm}$ thick. Figure 3 shows TEM for part of the cross section through a microtomed clay/polymer microsphere showing dispersed clay particles that appear to have similar dimensions. The separated clay particles, as shown in Figure 3, are typical of the clay particles found throughout the rest of the cross section of the microsphere and for other

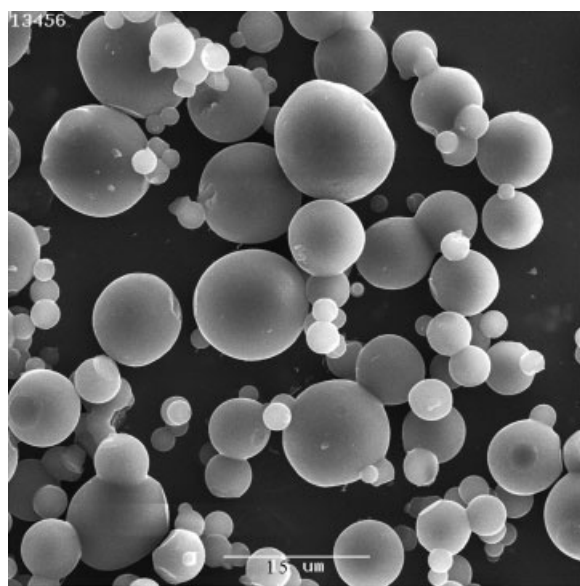


Figure 2 SEM image of spray-dried clay/polymer microspheres.

microsphere cross sections studied. They are also dispersed very homogeneously throughout the clay/polymer microsphere and are flexible, exhibiting a vast range of surface contours. From the thickness of their edges, the clays appear to be composed at most of a few platelets. Extensive (001) fringes, as seen by TEM when viewed side on, on clay particles composed of tactoids of many stacked clay platelets were not observed.^{6,7} The clay particles are therefore very unlike the original organoclay material, which consists of 5–10- μm particles (50% < 6 μm), each consisting of agglomerates of clay tactoids that themselves are composed of many tens of stacked platelets. From these SEM and TEM studies, it can be concluded that the spray-dry process produces clay/polymer microspheres in which the clay is trapped in a well-dispersed state throughout the polymer matrix.

Morphology of the bulk

The clay/polymer microspheres were extruded to give a bulk composite material (composite A) that was then subsequently studied with TEM and SAXS. From the TEM images in Figure 4, it can be seen that the clay particles are again composed of only a few platelets and on all accounts are very similar to those of the isolated clay/polymer microspheres, as observed by TEM, with some appearing faint with little contrast; this is indicative of their thin, delaminated nature. The fact that they have very curved contours, as well as very thin edges, indicates that they must generally be composed of less than three stacked clay platelets. In Figure 4(f), the particle on the far left is viewed edge on, and it appears that it is composed of three stacked

platelets (indicated between 2 arrows), each separated from the other by $\sim 3\text{--}4$ nm.

For the comparison of the morphology, a simple melt blend of the as-received polymer and raw organoclay material, with the organoclay 5% of the total weight, was extruded (composite B). Apart from good initial blending of the powders, no other pre-processing of the materials was performed. As can be

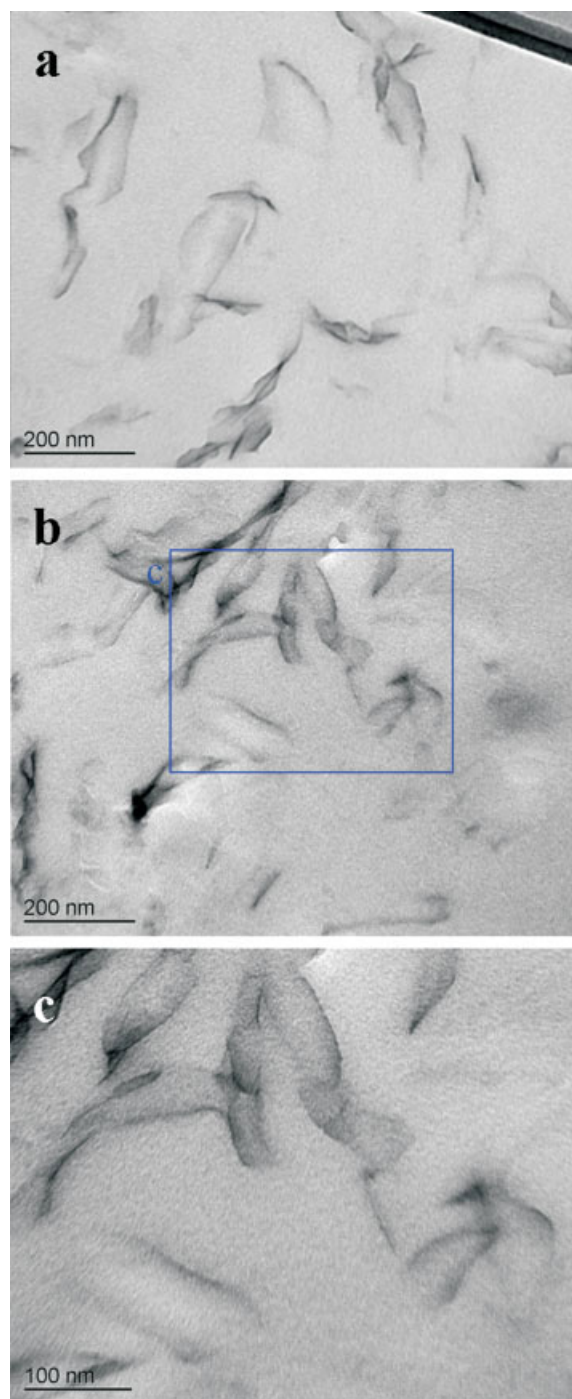


Figure 3 TEM images of clay/PMMA microspheres. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

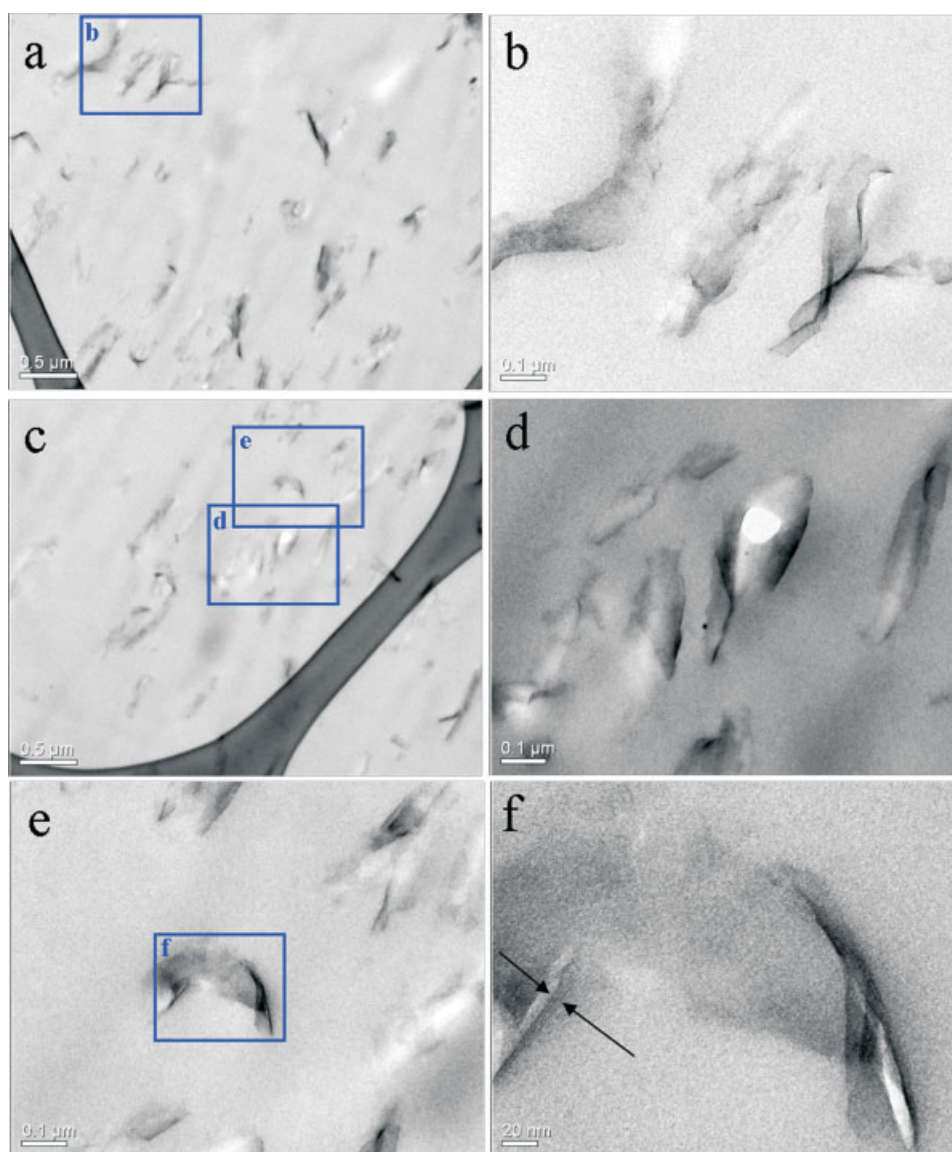


Figure 4 TEM images of nanocomposite bulk materials (composite A) extruded from clay/PMMA microspheres. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

seen in Figure 5, in contrast to the first extruded clay/polymer microsphere extruded material, large clay particles of the organoclay (5–10 μm), composed of agglomerated clay tactoids, remain, which are little broken up or separated by the extrusion process. Figure 5(a) shows a typical TEM image of a large tactoid in which many clay particles are essentially holding together after the extrusion. Figure 5(b) illustrates the high density of the aligned clay platelets within this large tactoid. Also shown in Figure 5(a) are smaller clay particles still composed of tactoids composed of many platelets. This is consistent with previous melt-blended PMMA–clay systems in which largely intercalation occurred and tactoids remained, showing only modest d -spacing increases of some 6.8 \AA ,⁸ whereas others have found increases of 8.8–15 \AA depending on the organo-treatment of the nanoclay.⁹

It can be concluded from the TEM images of Figures 3 and 4 that extrusion of the clay/PMMA microspheres has resulted in a nanocomposite material, whereas extrusion of the same organoclay and PMMA did not lead to such a finely dispersed nanocomposite. Indeed, the excellent degree of dispersion seen here for the clay/PMMA microsphere extruded material is more similar to the greater degree of dispersion seen in solvent-based nanocomposites.¹⁰ This is still, however, not always the case even with solution blending, in which very large tactoids can remain.¹¹

SAXS

The small-angle scattering technique provides structural information by averaging over a much larger sample volume than TEM and is therefore comple-

mentary to results of TEM. Figure 6 shows the SAXS curves in a log–log scale from the same two extruded materials (composites A and B) that were studied with TEM. When the clay is present as individual platelets, the slope of the data in a log–log plot is expected to be -2.0 , as it is for noninteracting thin discs.¹² It was shown that the deviation from Q^{-2} behavior resulted from the presence of tactoids.¹³ The slopes for the plots in Figure 6 are between -2.5 and -2.6 , and this is consistent with well-dispersed clays in suitable solvents and in polymer matrices.^{14,15} SAXS for composite A extruded from clay/PMMA microspheres shows a slightly smaller slope of -2.57 compared to that of -2.62 for composite B. The Bragg peak is more pronounced for composite B, clearly because of the remaining order in the clay, with the peak position corresponding to a d -spacing (i.e., $2\pi/Q^*$, where Q^* is the peak position) of 3.71 nm. The raw organoclay itself has a d -spacing of 1.85 nm, which indicates that considerable intercalation of the clay gallery with the polymer has happened to the organoclay in this extruded material. The additional small peak found at higher

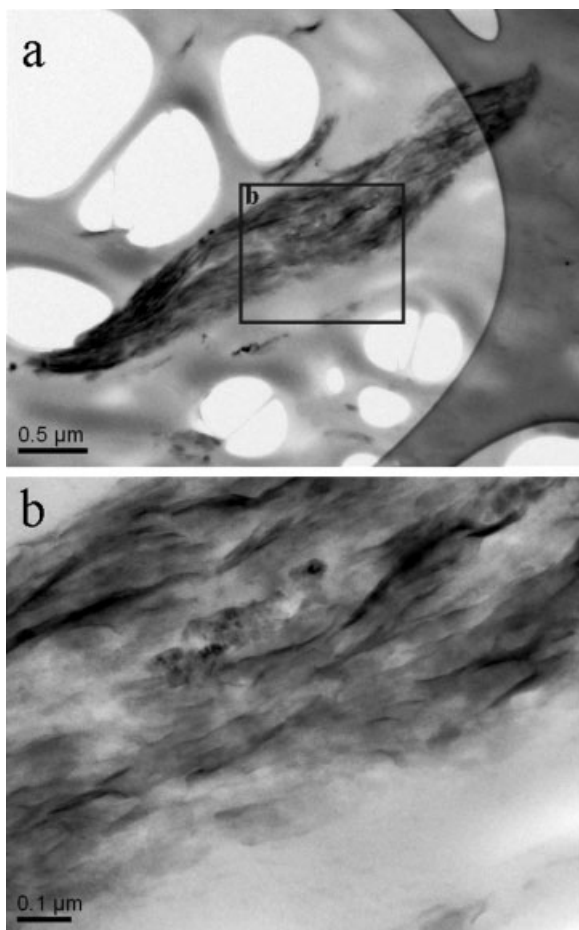


Figure 5 TEM images of nanocomposite bulk materials (composite B) extruded from raw clay and PMMA.

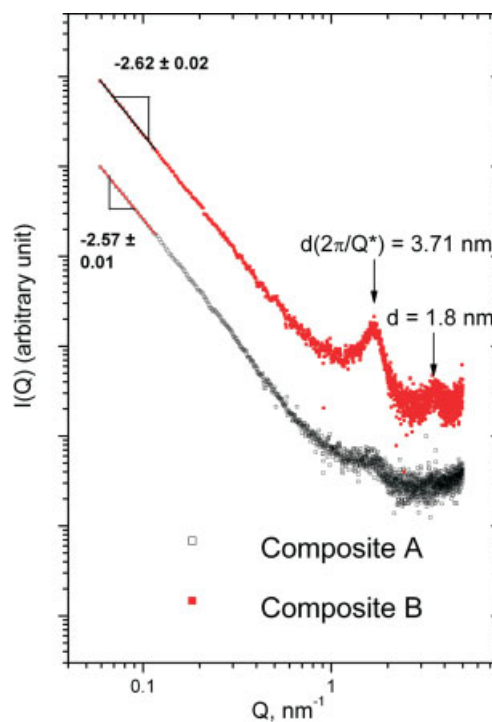


Figure 6 SAXS curves for nanocomposite bulk materials extruded from PMMA/clay microspheres (composite A) and mixture of raw clays and PMMA (composite B). The data for composite B have been shifted for clarity. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Q corresponds to a d -spacing of 1.8 nm, indicating that some nonintercalated clays still remain in composite B. In contrast, SAXS for composite A extruded from clay/PMMA microspheres shows only a very weak shoulder, which also contrasts with scattering data¹⁴ from an organoclay in toluene that showed a much more pronounced peak associated with tactoids consisting of up to 20 platelets. A high degree of exfoliation and small-sized tactoids consisting of only a few platelets (2–3), as shown by TEM, would result in a smaller number of total d -spacings present in composite A and therefore a weaker broader peak. The position of the shoulder corresponds to a d -spacing of 3 – 4 nm, agreeing well with the separation (3 – 4 nm) that was found for the three stacked platelets shown in Figure 4(f). SAXS therefore confirms what was observed with TEM, that the clay particles in this extruded material range from single platelets to simple tactoids composed of a few stacked clay platelets. Further study on quantitative analysis is under way with absolutely scaled small-angle neutron scattering data of nanocomposites.

CONCLUSIONS

New nanostructured microspheres that consist of organoclay and PMMA have successfully been

synthesized for the first time by the spray-drying method (indeed for any polymer/layered silicate pair). It has been found that the clay platelets are very uniformly dispersed throughout a microsphere. The rapid evaporation by spray drying effectively prevents any possible agglomeration of the clay tactoids initially present in the sonicated dispersion, which consists at most of only a few clay platelets. These tactoids in the nanocomposite exhibit a *d*-spacing of 3–4 nm, which is a result of intercalation by the polymer before spray drying. The microspheres were successfully extruded into clay/PMMA nanocomposite bulk structures without any perturbation of the well-dispersed nanostructure in the original microspheres. This means that these materials are very good precursors to further processing such as extrusion or melt blending with other polymers for bulk nanocomposite fabrication. Other advantages of the technique lie in the fact that spray drying is already a very understood and commonly used method in industry, so infrastructure development is minimized, and the technique allows for solvent recovery and can therefore be made environmentally safe and cost-effective.

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