

Rapid Communication

Suspension Polymerization of Methyl Methacrylate Stabilized Solely by Palygorskite Nano Fibers^{*}

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Abstract A kind of fibrous clay, palygorskite (PAL), was used as the sole stabilizer in suspension polymerization without the using of any other stabilizer usually used, especially polymeric stabilizers. In order to improve the compatibility with the organic monomer, PAL nano fibers were organically modified with silane coupling agent methacryloxypropyltrimethoxysilane (MPS). Transmission electron microscopy (TEM) and Fourier-transform infrared (FTIR) spectroscopy results show that the hydrolyzed MPS was attached onto PAL surface through Si—O—Si bonds formation without morphology change of PAL. At a loading amount of PAL to monomer as low as 0.36 wt%, effective stabilization could be achieved. After suspension polymerization, spherical poly(methyl methacrylate) (PMMA) particles were obtained. Scanning electron microscopy (SEM) analysis on both the outer surface and the inner cracked surface of the spherical PMMA particles indicates that the PAL particles reside on the surface of the PMMA spheres. The densely stacked PAL together with attached silane coupling agent stabilized the droplets throughout the suspension polymerization.

Keywords: Palygorskite; Attapulgite; Clay; Poly(methyl methacrylate); Suspension polymerization.

INTRODUCTION

Smectite clay minerals, especially montmorillonite (MMT), are most used platelet-type fillers for polymer clay composites. Addition of a small amount of such clay to pristine polymers imparts the resultant polymer clay nanocomposites with increased tensile strength and modulus, increased heat distortion temperature, increased smoothness and paint ability and increased transparency^[1, 2].

In recent years, clays showing non-lamellar structure arrangement such as tubular halloysite and imogolite, fibrous sepiolite and palygorskite (PAL) (also referred to as attapulgite), have become attractive as alternative nanofillers with an increasing use in the preparation of new nanocomposites^[3–6].

In the preparation of clay/polymer nanocomposites, in order to disperse hydrophilic clay minerals into hydrophobic polymer matrices, it is usually necessary to modify the surface of the clay particles to be organophilic. The sepiolite and PAL fibrous clays offer properties afforded by their unique morphological and surface structures that gives rise to the enhancement of mechanical properties associated with fiber reinforcement and interaction with matrix polymer through reaction of external reactive Si—OH groups. PAL and sepiolite are phyllosilicates inasmuch as they contain a continuous tetrahedral sheet; however, they differ from other layer silicates in that they lack continuous octahedral sheets. Their structure can be considered to contain ribbons of a 2:1 phyllosilicate structure, each ribbon being linked to the next inversion of SiO₄

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tetrahedra along a set of Si—O bonds. Thus, the tetrahedral apices point in opposite directions in adjacent ribbons. As the octahedral sheet is discontinuous at each inversion of the tetrahedral, oxygen atoms in the octahedra at the edge of the ribbons coordinate to cations on the ribbon side only, while coordination and charge balance are completed along the channels by protons, coordinated water and a small number of exchangeable cations. Furthermore, the channels contain a variable amount of zeolitic water. The periodic inversion of the tetrahedra silicon determines the presence of Si—OH groups on the external surface, and one of the advantages of fibrous clays as compared to layered silicates is the very high density of silanol groups^[3]. These silanol groups on the external surface are accessible to diverse organic species including coupling agents, organic surfactants and polymers, allowing the preparation of nanostructured organic-inorganic materials^[7, 8].

Suspension polymerization shows advantages, such as easy heat removal, low viscosity and particulate product, as compared with bulk or solution polymerization processes and has long been used commercially in the production polystyrene, poly(vinyl chloride) and poly(methyl methacrylate). When compared with emulsion polymerization, it shows advantages of lower level impurities and low product separation costs. In suspension polymerizations, the monomer phase is broken up into droplets under agitation and this agitation needs to be continued throughout the course of reaction. The size distribution of the initial monomer droplets, and hence the final polymer beads, is dependent upon the balance between droplet break-up and coalescence. Control of droplet coalescence is realized by use of different stabilizers. The stabilizers used are either water-soluble polymers, such as polyvinyl alcohol, methyl cellulose, and methyl-hydroxy-propyl-cellulose *etc.*, or inorganic particles, such as calcium carbonate, barium sulphate, aluminium oxide/hydroxide and various clays^[9]. Some of these stabilizers are hard to be removed from the final product.

Though particle stabilizers are commonly used in combination with low or high molecular surfactants in particle-stabilized suspension polymerizations, it is shown that stable suspension of oil in water could be achieved by solid particles after appropriate modification^[10–13]. But particle surface with much high oil phase compatibility would favor the complete immersion of solid particles in the oil phase^[13, 14]. The present work was aimed to explore the possibility of using PAL as the sole stabilizer of suspension polymerization without any use of polymeric stabilizer or surfactant. The fibrous PAL particles used can further serve as nano filler in the obtained product and thus the stabilizer removal processes can be excluded. For this purpose, PAL was modified by silane coupling agent through a simple aqueous process for a partly hydrophilic and partly hydrophobic surface property, the modified PAL was used as the sole stabilizer of the suspension polymerization of methyl methacrylate, of which the polymer is an important engineering material. Through suspension polymerization, PMMA particles in good sphere form were obtained.

EXPERIMENTAL

Materials

The monomer MMA of analytical grade was purchased from Tianjin Chemical Reagent Corporation Ltd. (China). Before use, the MMA was washed with 5 wt% NaOH aqueous solution for three times and then with water to neutral pH. MPS was purchased from Qufu Chenguang Chemical Corporation Ltd. (China) and used without further purification. Ammonia (25 wt%) and benzoyl peroxide of analytical grade was purchased from Tianjin Chemical Reagent Corporation Ltd. (China) and used directly. Purified PAL in powder form was supplied by Jiangsu Jiuchuan Nano-material Technology Corporation Ltd. (China). Deionized water was used throughout the experiments.

Organic Modification of PAL

0.5 mL of MPS was added to 80 mL water and the mixture was magnetically stirred for about 2 h to obtain a transparent solution of the hydrolyzate of MPS. 0.5 g PAL powder was added to the above solution under adequate stirring to make a uniform dispersion. Then, ammonia was added to adjust the pH to about 9 and the precipitation of white sediment was observed instantly. The sediment was collected by filtration and then re-dispersed in 20 mL water to make a milky dispersion of the modified PAL.

Suspension Polymerization

In a typical suspension polymerization process, 80 mL of water, 14.1 g of MMA and 0.2 g of benzoyl peroxide were added to a 250 mL flask, which was equipped with a mechanical stirrer and has a nitrogen inlet and an outlet. And then, 2 mL of the above silane modified PAL dispersion was added, which corresponded to 0.05 g of PAL. After bubbling nitrogen into the reactor for 30 min, temperature of the reactor was raised to 85 °C and kept at this temperature for 4 h and then raised to 95 °C for 1 h to make the reaction complete, with mechanical stirring applied in the whole process at about 500 r/min. When cooled to room temperature, the obtained suspension product was filtrated and then washed with water.

Characterization

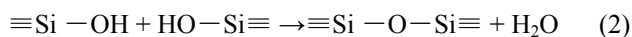
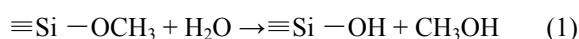
FTIR spectroscopy characterization of raw PAL and that treated with MPS was performed on a Spectrum One FTIR Spectrometer (Perkin-Elmer, USA), using KBr pellete method. Water contact angle determination of both raw and modified PAL was done by a flake method^[15], the flakes were made at 30 MPa. The sample of modified PAL was dried in air at room temperature for flakes and that of raw PAL was used as received, and the measurements were performed on a DSA100 contact angle analyzer (Kruss, Germany). TEM characterization was carried out on a TECNAI G2TF20 TEM (FEI, USA) at an accelerating voltage of 200 kV. Samples of aqueous suspensions of raw PAL and that treated with MPS were dropped on 300 mesh copper grid and used after drying in air. SEM observation of the morphology of palygorskite and suspension polymerization product was carried out on a JSM-6701F SEM (Japan). Samples of PAL and polymerization product PMMA were dispersed in ethanol and dropped on a glass plate. For observation of the inner phase of the obtained PMMA particles, the particulate sample of PMMA was crashed in liquid nitrogen in a porcelain crucible. All samples for SEM observation were sputtered with gold in vacuum.

RESULTS AND DISCUSSION

In suspension polymerizations, monomers are insoluble or slightly soluble in water. The monomer phase is broken up into droplets under continuous agitation shearing. Stabilizers are used to hinder the coalescence of monomer droplets. Efficient stabilizing effect could be realized when the stabilizer particles or molecules stay at oil/water interface. Hydrophilic inorganic particles have to be modified to make the surface hydrophobic. For the reason that pristine montmorillonite platelets can stabilize suspension polymerization of MMA^[16], in this study, as a comparison, raw PAL was first tried as the stabilizer. But serious agglomeration was observed and the reaction could not continue to complete.

Organic Modification of PAL with MPS

Water contact angle measurements show that after modification, the PAL gets more hydrophobic, with contact angle value of 7.3° for unmodified and 68.4° for modified PAL, respectively. This means that the modified PAL nano fibers tend to be adsorbed on oil/water interface because of its partly hydrophilic and partly hydrophobic nature. After organic modification with MPS, fibrous PAL nano particles successfully played the role of stabilizer without the addition of any other polymeric or inorganic stabilizer. Figure 1 shows the TEM image of unmodified PAL (Fig. 1a) and that modified with MPS (Fig. 1b). No obvious morphology change is found after MPS modification. In the present modification process, the methoxysil group $\equiv\text{Si}-\text{OCH}_3$ in MPS hydrolyzed to silanol group $\equiv\text{Si}-\text{OH}$. Catalyzed by the base ammonia, the intermolecular condensation reaction between methoxysil group and silanol group or between two silanol groups gave condensation product with different molecular weights, while particulate product that appears in basic conditions like that of methyltrimethoxysilane or tetraethoxysilane was not observed^[17, 18]. The hydrolysis and condensation reaction are simplified as follows^[19]:



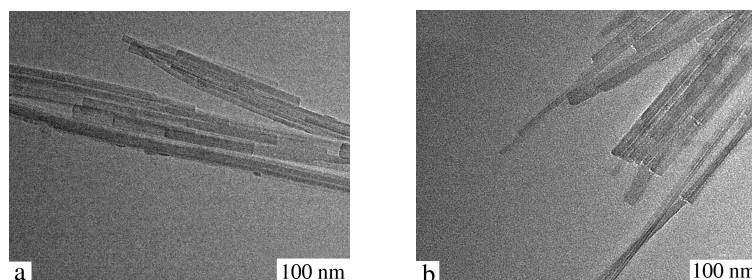
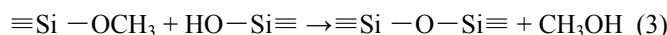


Fig. 1 TEM images of palygorskite before (a) and after (b) organic modification

Figure 2 shows the FTIR spectra of raw PAL, hydrolyzed MPS and modified PAL. In the spectrum of hydrolyzed MPS (Fig. 2a), the absorption bands at 2959 cm^{-1} and 2926 cm^{-1} are attributed to asymmetric stretching vibration of $-\text{CH}_3$ and asymmetric stretching vibration of $-\text{CH}_2-$ from MPS, absorptions at 1718 cm^{-1} and 1637 cm^{-1} are stretching vibrations of $\text{C}=\text{O}$ and $\text{C}=\text{C}$ in MPS, respectively. In Fig. 2(b) for the unmodified raw PAL, the band at 3739 cm^{-1} is attributed to the asymmetric stretching $-\text{OH}$ vibrations and that at 980 cm^{-1} the deformation vibration of the silanol groups located on the external surface of PAL^[20, 21]. The band at 3590 cm^{-1} is attributed to the coordinated water molecules in the channels and the band at 3556 cm^{-1} to the stretching vibration of $\text{Al}-\text{Fe}^{3+}-\text{OH}$ or $\text{Al}-\text{Mg}-\text{OH}$ band^[22]. After modification, the bands at 3590 cm^{-1} and 3556 cm^{-1} show no obvious change, meaning that the coordinated water and the hydroxyl groups in the channels were not affected by this modification process. Though the comparison of the bands at 3739 cm^{-1} of unmodified PAL (Fig. 2b) and that of modified PAL (Fig. 2c) shows no apparent change after modification, taking into consideration the additional absorption of MPS at 3739 cm^{-1} and decreased intensity of deformation vibration at 980 cm^{-1} , this means that intermolecular condensation between the silanol groups of hydrolyzed MPS and PAL did occur.

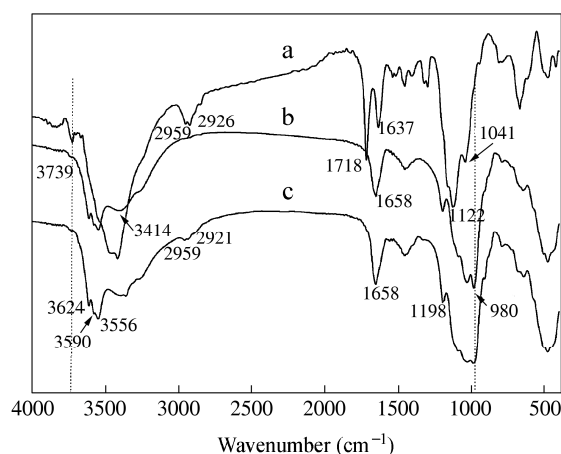


Fig. 2 FTIR spectra of hydrolyzed MPS (a), raw palygorskite (b) and organically modified palygorskite (c)

By combining the TEM images and the FTIR analysis, an organic modification mechanism is postulated here. During hydrolysis of MPS, reaction between $\equiv\text{Si}-\text{OCH}_3$ and silanol groups $\text{Si}-\text{OH}$ or between silanol groups leads to the formation of oligomeric condensation product and decreased solubility. As this reaction went on, the formed condensation product precipitated out from water and adsorbed onto the surface of PAL. Through formation of covalent bonds by the condensation reaction of hydrolyzed MPS with silanol groups on the surface of PAL and hydrogen bonds by $\text{C}=\text{O}$ from MPS with silanol groups on PAL^[23], the organic modifier is strongly attached onto the surface of PAL. This can be depicted simply in Fig. 3.

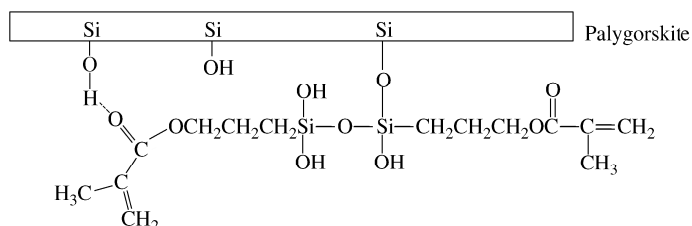


Fig. 3 Schematic show of the organic modification of palygorskite

Morphology of Suspension Polymerization Product

Figure 4 is the SEM image of unmodified raw PAL. It can be seen that most of the lengths of the PAL fibers are in the range of 1 μm to 2 μm . This size is larger than the radius of emulsion particles, which are usually less than 1 μm . A literature research of emulsion polymerization of MMA in the presence of PAL modified with cetyltrimethylammonium bromide only obtained PAL enwrapped with MMA or bead-string structure with PMMA beads adsorbed on PAL fibers^[24]. It implies that PAL particle in this size range is not suitable for use in emulsion polymerization as stabilizer, but it may be suitable for suspension polymerization stabilizing.

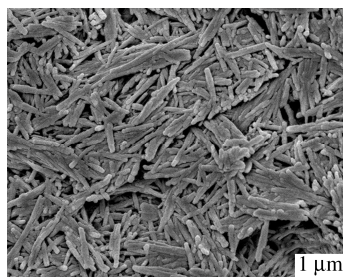


Fig. 4 SEM image of raw palygorskite

Figure 5 shows the SEM images of the suspension polymerization beads of PMMA stabilized solely by PAL treated with MPS. It can be found in Fig. 5(a) that the obtained PMMA particles are in good spherical shape. This means that the PAL stabilized MMA underwent a bead suspension polymerization process, in which polymer dissolved in its monomer and the monomer droplets passed through a viscous syrupy state before finally transformed into solid clear spheres.

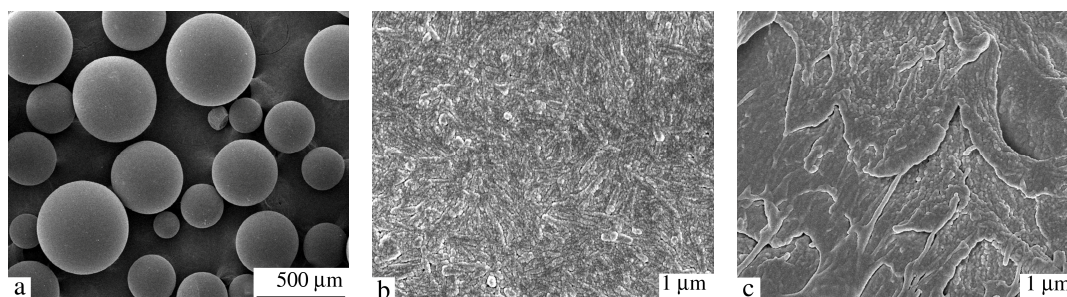


Fig. 5 SEM images of obtained PMMA spheres (a), stacking state of palygorskite on the surface of PMMA spherical particle (b) and cross section of PMMA particle (c)

An image with larger magnification of a localized surface (Fig. 5b) shows that the surface of the PMMA spheres is covered by densely stacked PAL nano fibers. These nano fibers at oil/water interface hindered the coalescence of the monomer droplets, especially at the sticky state of the droplets when the droplets transformed to polymer. Figure 5(c) is the image of cross section of the obtained PMMA beads for observing whether the

PAL nano fibers are dispersed in the inner phase of the PMMA spheres. From the cross section image (Fig. 5c), no extruded or broken fiber of PAL is observed, indicating that the PAL nano fibers reside only at the surface of the spherical particles. The amount of PAL used was very small, and the ratio of PAL to MMA is about 0.36 wt%. The effective stabilizing role the PAL played at a such small amount also implies that these nanofibers reside at the interface of the droplets of monomer^[25].

In the earlier stage of suspension polymerization, the stabilizer adsorbed at oil/water interface reduces interfacial tension and leads to smaller droplets on break-up. However, more significantly, the stabilizer forms an interfacial layer around the droplets, which reduces rate of coalescence by a steric stabilization mechanism. A thicker layer of stabilizer with higher dilational modulus may result in a more stable suspension^[26]. In the present case, the fibrous PAL particles act as stabilizer more efficiently than those spherical particles because of larger contact area with the surface of droplets and stronger interaction among these fibrous particles, which gives higher dilational modulus of the interfacial layer and a more stable suspension. On the other hand, the oligomeric organosilicon modifier attached on the surface of PAL plays part role of those polymeric stabilizers used in traditional suspension polymerizations, reducing the rate of radical diffusion from the droplet phase to continuous phase. This reduces the possibility of emulsion formation caused by monomer diffusion into water phase.

CONCLUSIONS

A kind of fibrous clay, PAL, was modified by coupling agent MPS in aqueous medium in a simple way. The modified PAL was used as the only stabilizer for MMA suspension polymerization, and stable suspension polymerization system was achieved, giving PMMA particles in good spherical form. SEM images show that the fibrous stabilizer particles reside at the surface of the PMMA particles. On the contrary, unmodified PAL could not stabilize MMA suspension polymerization effectively, meaning that this method is effective for PAL to act as stabilizer for MMA suspension polymerization. The present work has developed a new use of fibrous clay mineral as the sole stabilizer for suspension polymerization, which can be expected to be extended to other monomers.

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