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Original article

Fabrication of polymeric–Laponite composite hollow microspheres *via* LBL assembly

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ABSTRACT

Hollow structure microspheres with composite polymeric–Laponite shells were prepared by electrostatic self-assembly of Laponite on the polymeric hollow microspheres in this work. The multilayer hydrophilic core/hydrophobic shell polymer latex particles containing carboxyl groups inside were first synthesized *via* seeded emulsion polymerization, followed by alkali treatment, generating polymeric hollow microspheres. Then, polyethyleneimine (PEI) and Laponite were alternately electrostatic adsorbed on the prepared polymeric hollow microspheres to form polymeric–Laponite composite hollow microspheres. It was indicated that the morphology of alkali-treated microspheres could be tuned through simply altering the dosage of alkali used in the post-treatment process. Along with the increasing of the coating layers, the zeta potential of microspheres absorbed PEI or Laponite approximately tended to be constant respectively, and the thickness of Laponite layer around the hollow microspheres increased clearly, getting more uniform and homogenous. Furthermore, the corresponding polymeric–Laponite hollow microspheres showed high pressure resistance ability compared to the polymeric hollow microspheres.

1. Introduction

Microspheres with particular structure and function, especially hollow microspheres have stimulated great attention since the concept of particle design was proposed by Okubo in the 1980s. Due to their unique morphology and fascinating physical properties including large specific surface area, low density, excellent light scattering and accommodation for object, hollow microspheres displays broad application prospects in coating [1], electrode [2], catalysis [3], biomedical [4], and so on [5]. The combination of hollow structure with different materials such as polymeric, inorganic, metallic and biological materials has been intensively investigated [6–10]. Methods of preparing polymeric hollow microspheres reported over the past few decades ranged from osmotic swelling [11–13], assembly method [14,15], to SPG emulsification technique [16], as well as other polymerization-based approaches [17–20]. Among them, osmotic swelling technique based on emulsion polymerization is the earliest and predominant method, and its typical processes involves the synthesis of core/shell latex particles and the expansion of these particles through creating ions in the core under the appropriate conditions. However, the most literature of osmotic swelling technique is limited in patents due to the strong commercial interest of polymeric hollow microspheres, and it still needs improvement and development with the aim that polymer microspheres can be designed with unique hollow structure and controllable size. Sacrificial template is usually utilized to build inorganic hollow microspheres, and a final etching or calcining to remove the template is unavoidable [21–23], typically requiring the use of harmful solution or high temperature, which often leads to the cracking and aggregation of inorganic shells.

Current studies of hollow microspheres mainly focus on the homogeneous materials, such as polymeric hollow microspheres or inorganic hollow microspheres, and only little attention has been paid on the hollow microspheres with polymeric–inorganic composite shells, which enable materials to integrate the excellent properties of hollow structure with polymer as well as inorganic materials. Yang et al. [24] prepared hollow spheres with double-shelled and sandwiched composite structure by preprocessing the

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commercial polymeric hollow spheres and adsorbing the desired precursor. Liu et al. [25] reported the hollow inorganic–organic hybrid microspheres with the exterior silica shell and the interior poly(methacrylic acid) (PMAA) functionalized shell prepared based on the capillary force and the competitive hydrogen bond interaction. Teo et al. [26] investigated the influence of the monomer, cross-linker and initiator type on the synthesis of hollow polymer–graphene oxide particles *via* Pickering mini-emulsion polymerization.

In this work, we present an approach to prepare polymeric–Laponite composite microspheres with hollow structure inside by armoring Laponite directly on the surface of hollow polymer latex particles without any sacrifice of template. Hollow polymer latex particles with controllable morphology were prepared from synthesizing multistage hydrophilic core/hydrophobic shell latex particles and performing alkali post-treatment based on the osmotic swelling principle. Subsequently, composite polymeric–Laponite shells were formed by alternate adsorption of PEI and Laponite. The morphology, zeta potential and compression resistance of the hollow microspheres were studied. The results and approach represented an attractive route towards the preparation of such composite hollow microspheres.

2. Results and discussion

2.1. Preparation and morphology control of polymeric hollow latex particles

According to osmotic swelling principle, the preparation of hollow polymer latex particles began with the core/shell structure latex particles which were synthesized *via* seeded emulsion polymerization using carboxyl-containing core latex as seeds. During the whole polymerization process, the feeding speed of monomers was strictly controlled in order to decrease the local electrolyte concentration and increase the instantaneous monomer conversion. In addition, a polar intermediate layer was inserted to balance the polar difference between the hydrophilic core and hydrophobic shell, avoiding the mutual penetration of polymer chains and ensuring the preparation of designed core/shell structure [27]. The morphology of latex particles obtained at each stage was shown in Fig. 1, and microspheres with one, two and three layers could be clearly identified, corresponding to core, core/interlayer and core/interlayer/shell, with average diameter (Dp) of 126 nm, 178 nm and 251 nm, respectively.

When the core/interlayer/shell latex particles suffered alkali treatment, the carboxyl groups inside were ionized and water molecules permeated into the interior of latex particles due to the osmotic pressure, causing the volume expansion of latex particles. Our previous research work found that the alkali dosage had the most significant impact on the morphology of alkali-treated particles, followed by alkali post-treatment temperature, and the least effective for alkali post-treatment time [28]. By controlling the mole ratio of NaOH used in the post-treatment to MAA used in the polymerization ($MR_{\text{alkali/acid}}$) during the alkali post-treatment process, the alkali-treated microspheres presented different size and morphology, as shown in Fig. 2. It should be attributed to the different ionization degree of polymer chains at different $MR_{\text{alkali/acid}}$. When $MR_{\text{alkali/acid}}$ was 1.0, the ionized polymer chains generated by the neutralization were insufficient, only several small pores and little hollow structure with thick exterior covering were found in the alkali-treated particles. Along with $MR_{\text{alkali/acid}}$ climbed to 1.15 and 1.3, the increasing of ionized polymer chains promoted the osmotic swelling, leading to effective volume expansion and formation of uniform hollow structure with the shell thickness less than 60 nm and hollow ratio (Hr) higher than 45% (Fig. 2c). However, superfluous NaOH solution, such as $MR_{\text{alkali/acid}}$ reached 1.75, would bring deformed structure, which might result from the migration of some ionized polymer chains towards the water phase and the collapse of the thinning shell affecting together.

2.2. Assembly of Laponite on polymeric hollow microspheres

Layer by layer self-assembly technique allows the fabrication of monolayer and multilayer buildup on charged substrates by the sequential adsorption of oppositely charged materials. Both the resultant polymeric hollow microspheres and Laponite, a kind of synthetic hectorite-like clay, are surface negative charge, so PEI was used to modify the polymeric hollow latex particles shown in Fig. 2c, and the zeta potential turned from −45.1 mV to +44.9 mV after the adsorption of the cationic polyelectrolyte PEI. Directly mixing PEI modified polymeric hollow latex particles and Laponite in distilled water resulted in the irreversible precipitation even if the sample was drastically ultrasonic dispersed. It could be explained that charged microspheres tended to adsorb opposite charges around themselves to form large clusters if the electrostatic attraction between each microsphere was strong enough, and were easily precipitated out from the continuous phase along with the increasing of the volume. Stable emulsion system could be formed by using 0.1 mol/L NaCl solution instead of distilled water, because adding NaCl could squeeze the thickness of electric double layer of the colloidal particles and weaken the electrostatic attraction, which finally eliminated the risk of flocculation formation.

The morphology of polymeric hollow microspheres coated with different layers of Laponite was shown in Fig. 3. With the increasing of coating layers, the coating around the microspheres became more uniform and homogenous, and the thickness of clay increased, although no clear interface of each Laponite layer could be distinguished because of the extremely thin lamellar structure of Laponite. When three layers of Laponite were built up, the stacked clay around the surface of the hollow microspheres could be clearly identified, as shown in Fig. 3c. In order to further confirming the immobilization principle of Laponite on the polymeric hollow microspheres was based on the electrostatic adsorption, the surface charge of each step was characterized and

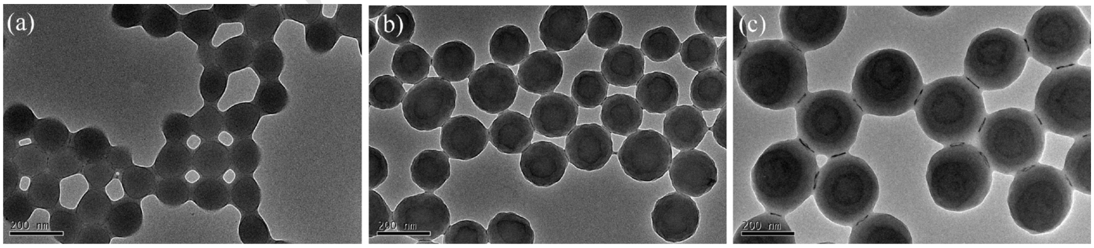

Fig. 1. TEM micrographs of microspheres prepared at each stage: (a) core, (b) core/interlayer, and (c) core/interlayer/shell.

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