

Preparation and Surface Modification of Non-porous Micron-sized Magnetic Poly(methyl acrylate) Microspheres

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Abstract: Micron-sized magnetic poly (methyl acrylate) (mPMA) microspheres were prepared by a novel modified suspension polymerization method. mPMA microspheres were highly functionalized by the ammonolysis reaction with ethylenediamine to yield abundant amino groups (-NH₂) on the surface. The morphology, magnetic property and surface functionality of the magnetic microspheres were examined by SEM, VSM and FTIR respectively. The results showed that the mPMA microspheres had average size of about 5 μm and superparamagnetic property. The micron-sized mPMA microspheres with amino functional groups have extensive potential applications in biotechnology such as enzyme immobilization and affinity separation.

Key words: magnetic microsphere, poly (methyl acrylate), surface modification, modified suspension polymerization

Introduction

Highly selective magnetic separations have found extensive applications in biotechnology and biomedicine, such as cell separation, enzyme immobilization and protein separation (Šafarik et al., 1999; Halling, et al., 1998; Hubbuch, et al., 1998). The technology is based on the immobilization of an affinity ligand on the surface of the magnetic carriers with functional groups. There are two main methods for the introduction of functional groups onto the polymer adsorbents. One relies on the copolymerization with monomers containing functional groups and the other is by chemical modification of performed polymer. The most often used is the former one. However, copolymerization always resulted in the low-density functional groups on the surface and most of the functional groups buried in the carrier. Various methods have been used to prepare magnetic microspheres, involving the coating of magnetic susceptible particles with natural and synthetic polymers, emulsion polymerization, suspension polymerization (Denkbas, et al., 2002; Yanase, et al., 1993; Lee, et al., 2003) and so on. Among these methods to prepare magnetic carriers, suspension polymerization is easy to perform and suitable for mass production. However, the magnetic microspheres obtained from conventional suspension polymerization are in the size of several hundred micrometers with broad size distribution. It is scarcely reported in literature that micron-sized (several microns) magnetic microspheres could be prepared with suspension polymerization.

In this study, we prepared non-porous micron-sized magnetic poly (methyl acrylate) (mPMA) microspheres by a novel modified suspension polymerization method. The resulting magnetic microspheres were highly functionalized via ammonolysis reaction with ethylenediamine (EDA) to yield abundant amino groups (-NH₂) on the surface. The morphology, magnetic property and surface functionality of the magnetic microspheres were examined by SEM, VSM and FTIR respectively.

Materials and methods

Materials

Methacrylate (MA) and divinylbenzene (DVB, used as crosslinker) were distilled under reduced pressure to remove the inhibitor before use. Benzoyl peroxide (BPO) was used as initiator. Poly (vinyl alcohol) (PVA-1788) was used as a stabilizer. All other chemicals were analytical grade and used without further purification, including ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ammonium hydroxide (25% [w/w]), oleic acid, dimethylformamide (DMF) and EDA.

Preparation of mPMA microspheres with modified suspension polymerization

The oleic acid-coated magnetite (Fe_3O_4) nanoparticles were first prepared by the co-precipitation method described before (Liu et al., 2003). Then the modified suspension polymerization of MA was carried out in the presence of oleic acid-coated magnetite nanoparticles. In a typical experiment, 95 ml MA was mixed with 5 ml DVB, 25 g magnetite nanoparticles and 4.0 g BPO to form the organic phase. 25 g PVA-1788 was dissolved in 800 ml deionized water. The above two mixtures were mixed to form suspension and then transferred to a 2-liter beaker equipped with four vertical stainless steel baffleplates, a condenser, a nitrogen inlet, and a 4-paddle stirrer. The polymerization was initiated at 45°C and increased to 60°C within 1 h and kept at 60°C for 2 h. Then the temperature was increased to 80°C and the reaction was carried out for 2 more hours with the stirring speed of 1000rpm. The resulting magnetic PMA-DVB microspheres were washed with ethanol and deionized water extensively to remove the excess of stabilizer and other impurities.

Surface modification of mPMA microspheres with EDA

2 g mPMA microspheres were added in 50 ml DMF solution containing 50% EDA. The mixture was stirred at 110°C for 12 h. The resulting amino-modified magnetic microspheres were separated magnetically and thoroughly washed with deionized water to remove excess EDA.

Characterization of magnetic microspheres

The size and surface morphology of mPMA microspheres were observed by scanning electron microscopy (SEM, JEOL JSM-6700F). The magnetization curves of the samples were measured with a vibrating sample magnetometer (VSM) (model-155, Digital Measurement System, Inc.). Surface functionality was characterized with the Fourier transform infrared spectroscopy (FT-IR, Bruker, Vector 22) using KBr pellets.

Results and discussion

Micron-sized mPMA microspheres were synthesized via a modified suspension polymerization method. The morphology and structure of the resulting microspheres observed by SEM are shown in Fig. 1. It can be seen that the microspheres are spherical in shape and eighty percent of the particles are in the size ranging from 1 to 5 μm . In order to obtain the micron-sized magnetic microsphere, three modifications were adopted in our study compared with conventional suspension polymerization. First,

the polymerization was conducted in a 2-liter beaker equipped with four vertical stainless steel baffleplates, so the droplets could be dispersed more uniform. Second, the reaction temperature was increased at a controlled rate. It is important to control the process of temperature increase to ensure the period of droplet dispersion and the formation of small droplets. Third, a large amount of PVA (25 wt% of monomer) was added in the dispersion medium, which was much higher than conventional suspension polymerization (1wt% of monomer).

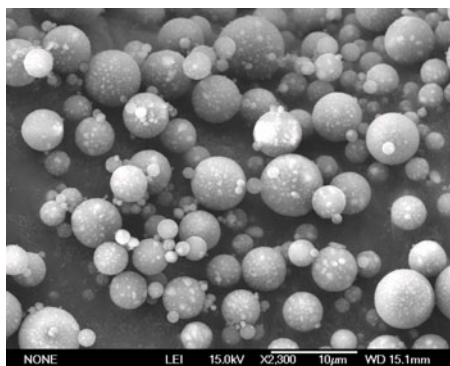


Fig. 1. SEM photograph of mPMA microspheres

The magnetic properties of the mPMA microspheres analyzed with VSM are shown in Fig. 2. The saturation magnetization was found to be 15.0 emu/g. There was no hysteresis observed, suggesting that the magnetic microspheres were superparamagnetic. The superparamagnetic property is critical for the magnetic supports used in bioseparation, which prevents magnetic particles from aggregation and enables them to redisperse rapidly when the magnetic field is removed.

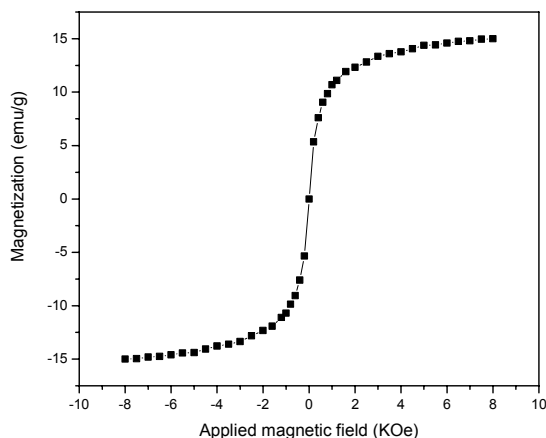


Fig. 2. Magnetization curve of the mPMA microspheres

The successful introduction of amino groups to the mPMA microspheres was proven by the comparison FTIR spectra of unmodified and EDA-modified mPMA microspheres. The results are shown in Fig. 3. The spectra of EDA-modified mPMA microspheres give some absorption bands different from those of unmodified mPMA microspheres. The most important absorption bands at 1650 cm^{-1} and 1545 cm^{-1} represent amide \square (C=O stretching) and amide \square (N-H bending), respectively, are due to EDA bonded to mPMA microspheres.

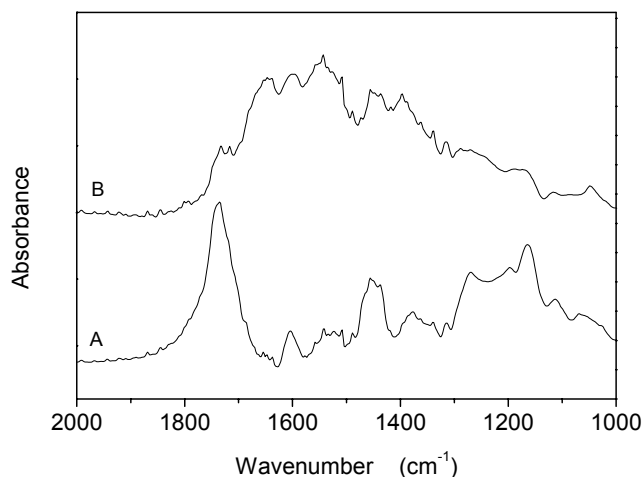


Fig. 3. FTIR spectra of unmodified (A) and EDA-modified mPMA microspheres

Conclusions

Micron-sized mPMA microspheres with non-porous structure were prepared by modified suspension polymerization. The mPMA microspheres had an average size of 5 μm and relative narrow size distribution. With the saturation magnetization of 15.0 emu/g and superparamagnetic characteristics, the magnetic microspheres could be easily separated from the solution and redispersed with the magnetic field removed. After modification, mPMA microspheres became more hydrophilic and the amino groups were useful, after activation, for immobilization of enzymes and coupling of amino-group containing affinity ligands. Moreover, these microspheres were non-porous, thus had better mass transfer and were less prone to fouling. Micron-sized mPMA microspheres have great potential applications in biotechnology and bioseparation.

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