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A novel method for the synthesis of polyamide 6 magnetic microspheres

Yan Liu · Tingxiu Xie · Guisheng Yang

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Abstract Polyamide 6 (PA6) magnetic microspheres were firstly prepared via successively in situ polymerization using phase inversion technology of polymer pairs polyamide 6/polystyrene (PA6/PS) at extremely low PS content. The properties of PA6 magnetic microspheres, such as morphologies, diameter size distribution, magnetic properties, thermal stability, and the functional groups of the magnetic microspheres, were investigated by different techniques (i.e. SEM, TEM, DLS, VSM, FTIR, and DSC). The results indicated that the diameter distribution of PA6 magnetic microspheres was narrow, and the mean diameter size was about 7.7 μm. The saturation magnetization of magnetic microspheres reached 12.50 emu/g. Furthermore, the magnetic microspheres had abundant functional groups and better thermal stability.

Introduction

Magnetic polymer microspheres are generally applied for magnetic carrier technology. The most popular application of magnetic carrier technology is wastewater treatment, immobilization of enzymes or other biomolecules and the preparation of immunological assays [1–5]. Magnetic carriers are most commonly prepared from polymers, since they have a number of actively functional groups, which can be tailored to specific materials with desired properties. In the literature, different types of polymers, such as polystyrene [6], polyacrylamide [7], polyvinyl alcohol [8], poly(glycidyl methacrylate) [9], and poly(methylmethacrylate) [10] have been used in the preparation of magnetic carriers. However, polyamide 6 (PA6) is one of the important engineering plastics with excellent solvent resistance and abundant active groups (amide groups) [11], few researches on the synthesis of PA6 magnetic microspheres with Fe_3O_4 particles via successive in situ polymerization have been reported yet.

In our previous study [12], an alternative method for preparation of PA6 microspheres with regularly spherical shape and controllable size are explored. To further apply the technology and widen the PA6 microspheres application fields, the ferroferric oxide (Fe_3O_4) particles are added in the mix monomer St/CL system via successively in situ polymerization in one reactor, which obtain the PA6 magnetic microspheres. Importantly, the phase inversion occurs at an extremely low PS content (15 wt%).

In this article, the mass ratio of monomer of polymer pairs PA6/PS is selectively 80:20 due to narrower size distribution and regular shape. The mass of Fe_3O_4 particles is intended to be 10 wt% of total mass of styrene and ε-Caprolactam monomer (CL) in view of polymeric viscosity of CL and appropriately magnetic property. The solvent used to dispose the microspheres can be recycled. The dissolved PS can be reclaimed for utilization. The PA6 microspheres are not observed in other PA6/PS system with low PS contents via conventional melt mixing method [13–16]. Moreover, the Fe_3O_4 particles are located in the PA6 microspheres' phase. Therefore, the method used for the preparation of PA6 magnetic microspheres shows the advantage for commercialization.

Y. Liu · G. Yang (✉)
Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, Zhejiang, China
e-mail: ygs20082008@gmail.com

T. Xie · G. Yang
Shanghai Genius Advanced Materials Co., Ltd,
Shanghai 201109, China

Experimental

Materials

ε-Caprolactam monomer (CL) was bought from Nanjing Oriental Chemical Company (Commercial-grade, China). Azodiisobutyronitrile (AIBN), sodium hydroxide (NaOH), tetrahydrofuran (THF), methylene dichloride, and 2,4-toluene diisocyanate (TDI) (Analysis purity) used in this study were all purchased from Shanghai Chemical Reagents Co. and used without further treatment. Styrene was distilled at 45 °C under vacuum and reserved at −20 °C. Fe_3O_4 particles were supplied by Nanjing Emperor Nano Material Co., Ltd. (China).

Preparation

MCPA6/PS/Fe_3O_4 ternary composites were prepared following the two steps:

(1). Distilled styrene was dispersed in melted CL monomer at 80 °C with the weight ratio of 20:80, and a homogeneous pellucid mixture was generated. Then, 0.2 wt% AIBN was added and kept stirred for 24 h at 80 °C under nitrogen for the polymerization of styrene. After it, a clear and viscous mixture PS/CL was obtained.

(2). A certain amount of Fe_3O_4 particles (the mass is 10 wt% of total mass of styrene and CL) was added to the above mixture. After this, 0.4 wt% NaOH was added with stirring, and vacuumed at 120 °C for 20 min to remove trace amount of the water and then 0.4 wt% TDI was added with stirring. The mixture was then immediately poured into a mold preheated to 160 °C and polymerized in an oven at 160 °C for 20 min.

(3). After the composite obtained being crashed coarsely, the PS matrix was dissolved adequately with THF and the solution was filtered with a tundish, then the products obtained were put into water and separated from an adscititious magnetic field. Then, the PA6 magnetic microspheres were obtained. Pristine PA6 microspheres were synthesized under the same reaction conditions as above without adding Fe_3O_4 particles.

Characterization

The blend morphologies were examined by field emission scanning electron microscope (FESEM, JSM-6360LV, JEOL). The cryo-fractured surface of samples in liquid nitrogen was etched by THF for 12 h, and sputtered with gold prior to SEM examinations.

Transmission electronic microscopy (TEM) was carried out on a Hitachi H-800 microscope at an acceleration voltage of 90 kV. The samples were ultramicrotomed with a diamond knife on a Leica Ultra cut UCT microtomed at −20 °C to give 70 nm thick sections.

The magnetic properties of the PA6 microspheres were measured by vibrating sample magnetometry (VSM, LDJ9600-1, LDJ, USA) at room temperature (25 °C).

The functional groups of PA6 magnetic microspheres were confirmed by Fourier transform infrared spectrometry (FTIR) on pellets of KBr with small quantities of the sample.

The particle size was measured in dichloromethane using a Brookhaven dynamic laser light scattering system (DLS) consisting of a BI-200SM goniometer and a BI-9000AT digital correlator. A 532 nm vertically polarized argon ion laser was used as the light source. The measurements were carried out at 90° scattering angle at 25 °C. Sizes are given as the means of five runs ± standard deviation.

Differential scanning calorimeter (DSC) measurements were carried out on an NETZSCH DSC 200 PC calibrated by In standards. All the measurements were firstly performed from room temperature to 260 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere and held at that temperature for 5 min to remove any previous thermal history. A second heating scan was carried out.

A Waters-991 gel permeation chromatography (GPC) instrument was used to evaluate the number-average molecular weight $\left(\overline{M}_n\right)$, weight-average molecular weight $\left(\overline{M}_w\right)$ and their polydispersity indices $\left(\overline{M}_w/\overline{M}_n\right)$ of the samples, by calibration with a PA6 standard. The measurements were performed at 35 °C on polymeric solutions in *m*-cresol ($c = 0.5$ g dL^{-1}). All samples were dissolved by *m*-cresol and were filtered through a 0.2 mm filter in order to remove the Fe_3O_4 particles. The MCPA6 in the filtrate was precipitated by acetone and dried in the vacuum at 80 °C for 12 h.

Results and discussion

SEM observation

Figure 1 shows the cryo-fractured surface of the MCPA6/PS/Fe_3O_4 blends performed etching with THF on different magnification. SEM photographs of the cryo-fractured surface of the ternary blends obtained via successive in situ polymerization show quite characteristic morphologies differing from other melting blends (i.e., PA6/PS), and PA6 forms the dispersed microspheres with diameter size about 5–10 μm. In this study, once the PS content is higher than 15 wt%, phase inversion starts up, and the phase

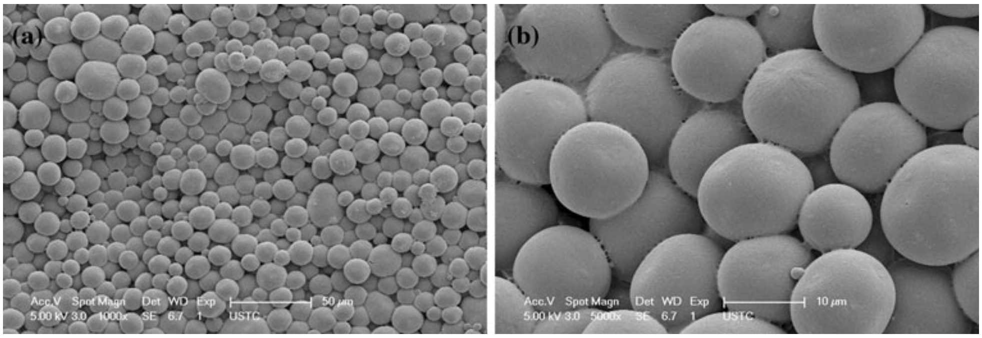

Fig. 1 SEM images of the fractured surface of composite (**a**) and its corresponding magnifying image (**b**) etched by THF

morphologies of the PA6/PS blends gradually change from the PS dispersed/PA6 matrix to PA6 dispersed/PS matrix system. Further details can be found in our previous article [12]. This was proven by using selective solvents [17]. For the blends, THF is a good solvent for PS phase, whereas formic acid is a good solvent for PA6 phase. Here, THF is selected to etch the PS phase. After that, the fractured surface of the blends exhibits a dispersed microsphere structure, and it is doubtless that the dispersed microspheres are PA6 microspheres. In this work, it is interesting to find that Fe_3O_4 particles locate selectively in PA6 microspheres due to good interfacial affinity between Fe_3O_4 particles and polar chains of PA6. It is found that most of microspheres contain the Fe_3O_4 particles. After dissolving the PS continuous phase, the microspheres are separated by an adscititious magnetic field. The pure PA6 magnetic microspheres are obtained. Figure 2a and b displays the pure PA6 microspheres and PA6 magnetic microspheres, respectively. In the same magnification factor, the size of the magnetic microspheres is more than that of PA6 microspheres. It is likely attributed to the Fe_3O_4 particles enhance the viscosity of the CL component, the flowing PS cannot break the PA6 up to little droplets in the process of fast anionic polymerization. To further indicate selective dispersion of the Fe_3O_4 particles in blends, TEM characterization will be adopted in the next section.

TEM observation

Figure 3 shows TEM micrographs of the dispersed state of the Fe_3O_4 particles in the blends. The sphere shape was PA6 phase and black particles were Fe_3O_4. It is obvious that Fe_3O_4 particles dispersed in the PA6 sphere phase (Fig. 3a) and the edge of the PA6 microspheres (Fig. 3b), and this further confirms the selectively location of Fe_3O_4.

Magnetic properties

For PA6 magnetic microspheres, magnetic hysteresis loops are important parameters. Figure 4 shows a typical magnetic hysteresis loop of PA6 magnetic microspheres at room temperature (25 °C). The saturation magnetization of these microspheres is about 12.50 emu/g. Two values are present as 2.3 emu/g and 180 Oe for remanence and coercivity in Fig. 4, respectively. As it can be seen, a 500 Oe magnetic field was found to be sufficient to excite almost 60% the dipole moments of 1 g magnetic microspheres. The magnetic microspheres are considered paramagnetic because of the magnetic susceptibility greater than zero. As the particular method of preparation used in this work, the PA6 molecular chains firmly wrap up the Fe_3O_4 particles. And that PA6 posses excellent solvent resistance, wearing capacity and abundant active groups (the same functional groups namely amide in their main

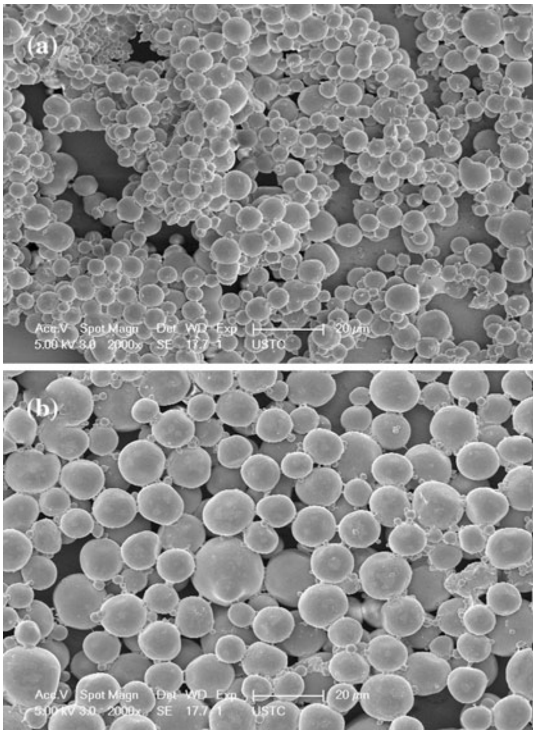

Fig. 2 SEM images of **a** the pure PA6 microspheres and **b** magnetic microspheres

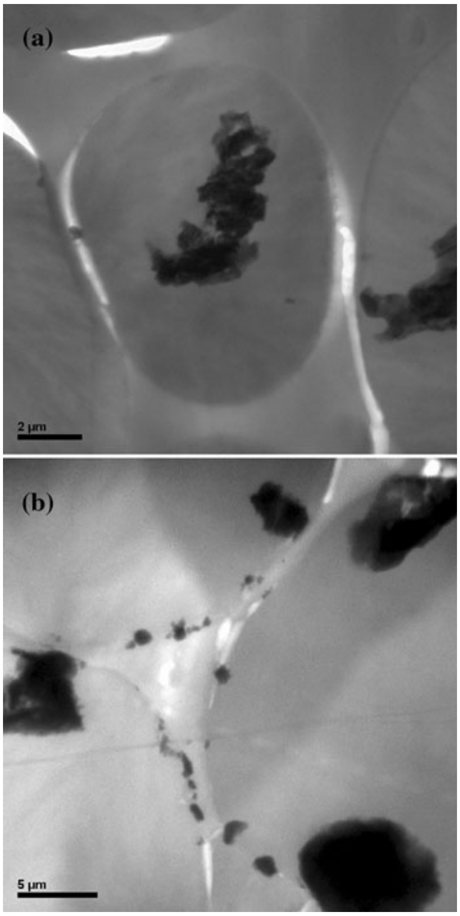

Fig. 3 TEM micrographs of the dispersed state of the Fe_3O_4 particles in the blends

chains), moreover, the PA6 magnetic microspheres can be easily and quickly separated from a suspension by an adscititious magnetic field. Figure 5a shows the image of the dichloromethane suspension solution contained magnetic microspheres. Figure 5b reveals that the magnetic microspheres are all separated in the suspension solution by an adscititious magnetic field after several minutes, and the solution changes clear. Hence, PA6 magnetic microspheres will explore a favorable market prospect in several of fields, such as protein immobilization [18–22], drug carrier [23, 24], and wastewater treatment [25, 26].

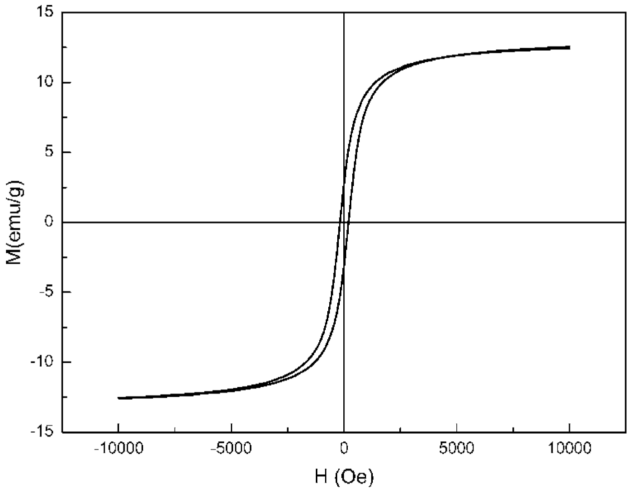

Fig. 4 Magnetic hysteresis loops for PA6 magnetic microspheres

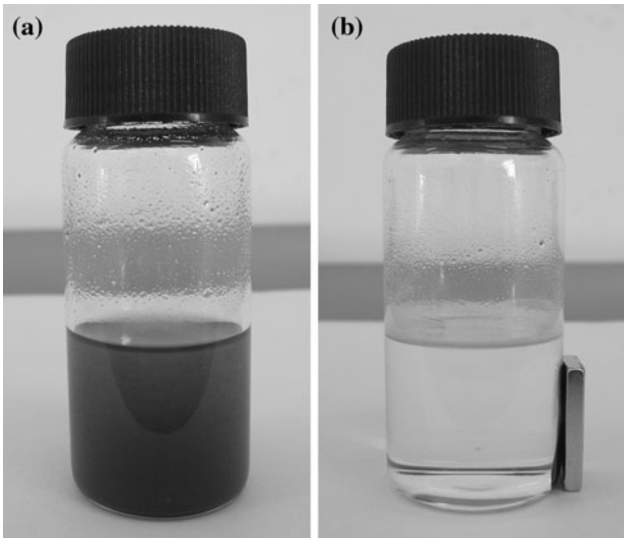

Fig. 5 Comparison images of **a** magnetic microspheres suspension solution and **b** magnetic microspheres solution by an adscititious magnetic field

Functional groups

The functional groups of PA6 magnetic microspheres are very important for diverse applications. The chains of PA6 pack the magnetic Fe_3O_4 particles via phase inversion of successive in situ polymerization. Figure 6 shows the FTIR spectra of Fe_3O_4 particles, pure PA6 and PA6 magnetic microspheres. In Fig. 6a, the characteristic absorption band of Fe_3O_4 particles appears at 580 cm^{-1} [27], and it also appears in the spectrum of PA6 magnetic microspheres (Fig. 6c). In Fig. 6b, the band at 1,642 cm^{-1}, which corresponds to the stretching vibration of the C=O group, typical of the amide group [28]. The band at 1,536 cm^{-1} caused by the flexion vibration of the N–H group combined to tension of the C–N group [16]. They also present in the spectrum of magnetic microspheres. These results further indicate that the functional groups ($-NH_2$) are presented on the microspheres' surfaces and Fe_3O_4 particles are located in the PA6 sphere phase. Here due to PS is non-polar, while PA6 and Fe_3O_4 particles are polar, there is a special absorption interaction between PA6 chains and Fe_3O_4 particles which causes the favorable compatibility in the interphase of them. It is just the preferential location

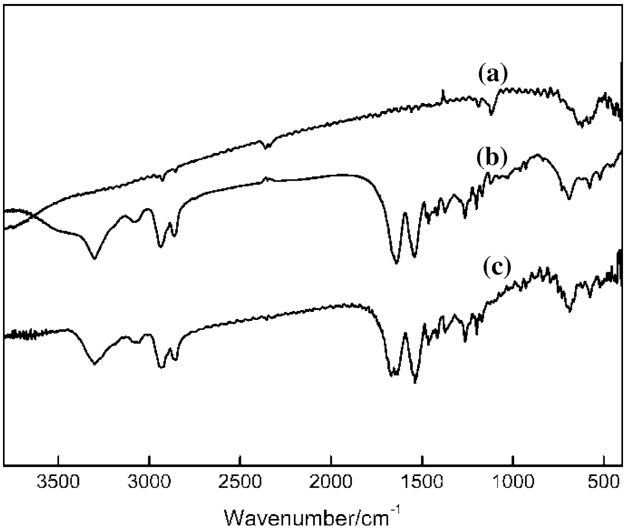

Fig. 6 FTIR of **a** Fe_3O_4, **b** pure PA6, and **c** PA6 magnetic microspheres

behavior [29, 30] that enable possible to obtain the PA6 magnetic micropspheres. Active groups existed in PA6 magnetic microspheres are easily adorned, and which can easily expand the application fields of magnetic microspheres.

DLS measurements

The diameter size of the PA6 magnetic microspheres was measured by Dynamic light scattering instrument. As shown in Fig. 7, it has much narrower size distribution. The particle size distribution of the product magnetic microspheres varies in size from 3 to 14 µm with a mean diameter of about 7.7 µm, which is well in accordance with the results from SEM.

Thermal stability

The cooling thermograms of the PA6 magnetic microspheres are presented in Fig. 8a. The crystallization temperature of the magnetic microspheres is 186.1 °C. In Fig. 6a, the half peak width of the crystalline peaks ($W_{1/2}$) of PA6 magnetic microspheres (6.3 °C) narrowed, compared with that of pure PA6 microspheres (9.1 °C), which indicates that the ability to crystallize improved owing to the addition of Fe_3O_4 magnetic particles. This suggests that well-dispersed Fe_3O_4 magnetic particles could act as a heterogeneous nucleation agent for the MCPA6 matrix and enhance its crystallization rate. The second heating DSC traces are presented in Fig. 8b. There are two peaks at 213.0 and 220.0 °C for MCPA6 magnetic microspheres, respectively. The values are all increased than pure PA6

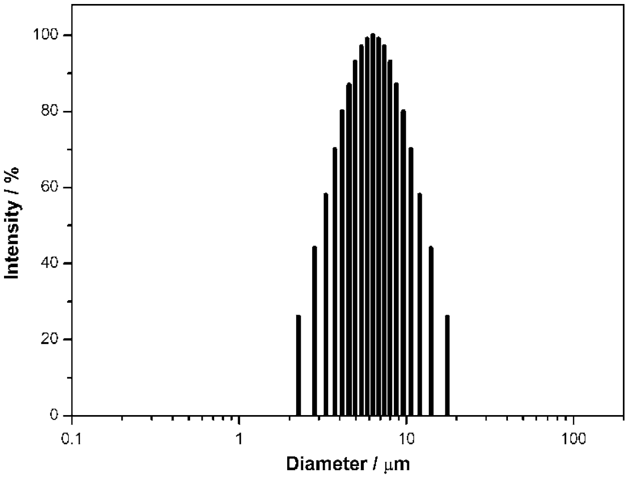

Fig. 7 The size distribution of PA6 magnetic microspheres

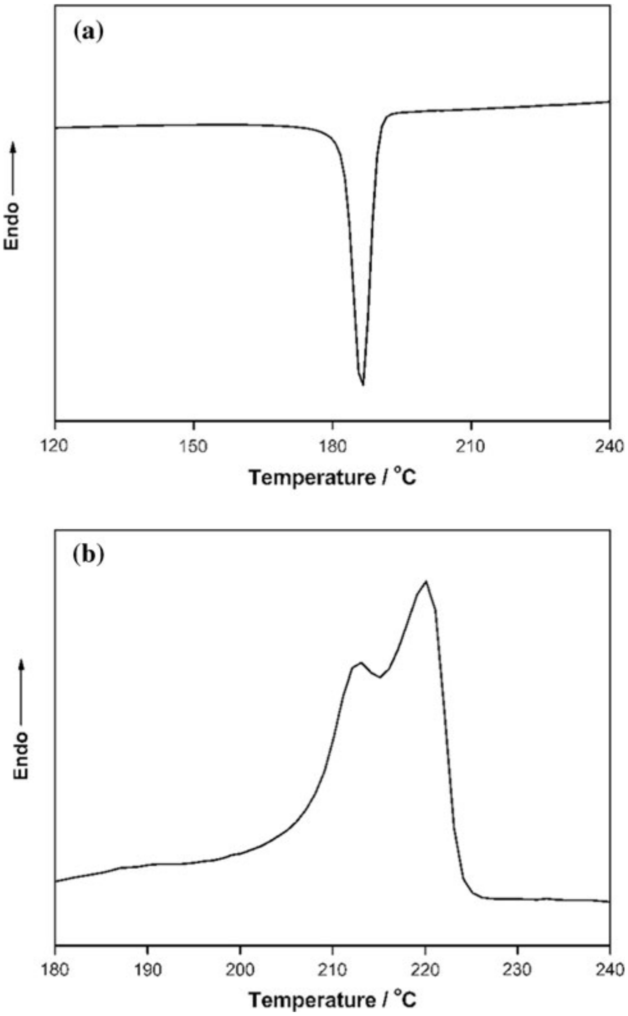

Fig. 8 DSC thermograms of PA6 magnetic microspheres, **a** cooling and **b** the second heating

Table 1 $\overline{M}_n$,$\overline{M}_w$ and polydispersity index (D) for PA6 microspheres and PA6 magnetic microspheres

Samples	Conversion (%)	$\overline{M}_n$ kg mol^{-1}	$\overline{M}_w$ kg mol^{-1}	D $\overline{M}_w/\overline{M}_n$
PA6 microspheres	94	19.1	52.2	2.74
PA6 magnetic microspheres	95	15.5	22.1	1.42

microspheres. These results demonstrated that the PA6 magnetic microspheres have a better thermal stability.

GPC results

Monomer conversion, number-average molecular weight ($\overline{M}_n$), weight-average molecular weight ($\overline{M}_w$), and distribution ($\overline{M}_w/\overline{M}_n$) of PA6 microspheres and PA6 magnetic microspheres are given in Table 1. $\overline{M}_w$ and $\overline{M}_n$of PA6 magnetic microspheres are lower than that of PA6 microspheres. The main reason can be explained as follows: addition of Fe_3O_4 particles located selectively in the CL phase increases the viscosity of the CL, and as a result, the reactive activity of CL monomer decreases [31]. However, the distribution D of PA6 magnetic microspheres is lower than pure PA6 microspheres.

Conclusions

In this study, PA6 magnetic microspheres were prepared by a novel successive in situ polymerization technique. The morphologies of composites were studied by SEM and TEM, which demonstrated that PA6 formed a dispersed microspheres' phase, Fe_3O_4 particles selectively located in PA6 microspheres. The mean diameter of magnetic microspheres was about 7.7 μm and its size distribution was narrow according to DLS results. The magnetic properties of microspheres were studied by VSM, which indicated that the saturation magnetization reached 12.50 emu/g. It can be separated from suspension solution easily by an adscititious magnetic field. The magnetic microspheres had abundant functional groups and better thermal stability according to FTIR and DSC. As an excellent engineering plastic, PA6 based on microspheres was endowed with magnetic property, which could be useful potential of high technology, such as affinity separation of biomolecules, diagnostic applications, and wastewater treatment.

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