

Fe₃O₄ / Thermo-Responsive Polymer Composite Nanofibers

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Introduction

One-dimensional nanostructures in the form of fibers have attracted plenty of attention due to their novel properties and applications in many areas in the past years [1]. Nanofibers have found use in a broad range of applications owing to their low dimensions and large surface areas. Magnetic nanoparticles known as Fe₃O₄ can be controlled by external magnetic field and have been used in plenty of field, such as environment, biology, biomedical applications, etc. Poly(N-isopropylacrylamide) (PNIPAAm) is a well-studied biocompatible and thermo-responsive polymer, which undergoes a sharp and reversible phase transition between hydrophilicity and hydrophobicity at 32 ± 1-2°C. In this study, Fe₃O₄ / thermo-responsive polymer composite nanofibers were fabricated by electrospinning successfully, and their thermal and magnetic properties were studied.

Experimental

Materials

Fe₃O₄ nanoparticles were synthesized by coprecipitation of Fe(II) and Fe(III) salts in aqueous solution of ammonium hydroxide. In this process, 23.5g of FeCl₃·6H₂O and 8.6g of FeCl₂·4H₂O were dissolved in 400mL deionized water with stirring. Then 50mL of 28% ammonium hydroxide solution was added. After reaction at 25°C for 6 min, the Fe₃O₄ nanoparticles were obtained. Subsequently, 2.5g of lauric acid was added to the above Fe₃O₄ solution and the condensation reaction could be done at 90°C for 30min. Finally, double-layer lauric acid modified Fe₃O₄ (DLF) nanoparticles dispersed well in water were fabricated [2]. The concentration of DLF solution was measured gravimetrically after sedimentation under magnetic field and drying. PNIPAAm homopolymer was synthesized using redox initiation. During this process, the polymerization reaction was kept at 28°C for 1 day. Later, the polymer solution was dried in the

oven for 50°C and PNIPAAm powder could be obtained. DLF/PNIPAAm polymer solutions with different composition were prepared by mixing appropriate amount of DLF solution, PNIPAAm and deionized water. After drying the mixture in the oven, DLF /PNIPAAm composite was fabricated. Samples for DSC measurement and electrospinning were prepared by desolving DLF/PNIPAAm composite in adequate deionized water and ethanol respectively. PNIPAAm content of all samples for electrospinning is 10 wt% in ethanol.

Characterization and electrospinning

The image of DLF nanoparticles was observed by TEM (Hitachi H-7100). Fe₃O₄/PNIPAAm weight ratio was estimated by TGA (Perkin-Elmer TGA 7) with heating rate of 20°C/min from 100 to 800 °C. Lowest critical solution temperature (LCST) of DLF/PNIPAAm aqueous solution was measured by DSC (Perkin-Elmer Pyris 6) with heating rate of 2°C/min from 5 to 45 °C. In electrospinning process, working distance, voltage, and injecting rate were set to be 15cm, 16.5kV, and 0.4mL/hr respectively. Appearance of electrospun nanofibers was observed by SEM (JEOL JSM-6700F). The magnetization of Fe₃O₄/PNIPAAm composite nanofibers was measured from -10000 to 10000 Gauss at 300K by SQUID magnetometer (Quantum Design MPMS-7).

Results and Discussion

The TEM picture of DLF nanoparticles is shown in Fig.1a. The size of Fe₃O₄ nanoparticles is around 10 nm. The TGA analysis was performed for different DLF/PNIPAAm composite samples. Table 1 shows the relationship between composition of samples and the weight of residue at 800°C from TGA. The weight of residue from TGA is proportional to the content of Fe₃O₄ in the composite samples. Interaction between DLF nanoparticles and PNIPAAm was investigated by measuring the shift of LCST for different composite samples with DLF content

Sample	DLF solution (g)	PNIPAAm 10 wt %(g)	DLF content in DLF/PNIPAAm composite	Weight of residue from TGA
PNIPAAm		2	-	-
DLF/PNIPAAm 1	1	2	2.0 wt%	1.8 wt%
DLF/PNIPAAm 2	2	2	3.8 wt%	2.8 wt%
DLF/PNIPAAm 3	3	2	5.6 wt%	4.8 wt%

Table 1 Compositions of DLF/PNIPAAm composite and weight of residue from TGA at 800 °C

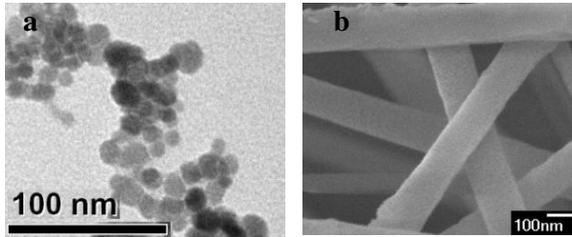
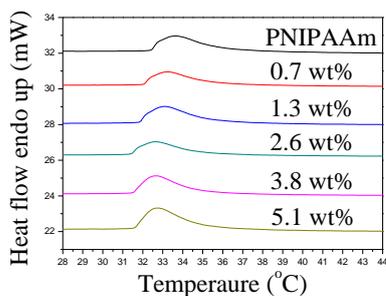


Fig.1 (a) TEM image of DLF nanoparticles (b) SEM image of nanofibers with 5.6wt% of DLF content in DLF/PNIPAAm composite

from 0 to 5.1 wt%. LCST of PNIPAAm measured by DSC is 32.5°C which is determined to be the onset of the endothermic peak (Fig.2). The LCST shift of DLF/PNIPAAm solution is related to the interaction between carboxylic acid groups on DLF and amide groups on PNIPAAm. The hydrogen bonding between PNIPAAm and H₂O was influenced by the interaction between DLF and PNIPAAm. For this reason, LCST of DLF/PNIPAAm solution decreases gradually with increasing the content of DLF.

Fig. 2 Heat flow of phase transition during heating using DSC. All samples were aqueous solution with 15 wt% of PNIPAAm in H₂O. Compositions of DLF content in DLF/PNIPAAm composite were from 0.7 wt% to 5.1 wt%.

In the process of electrospinning, PNIPAAm content of all samples is 10 wt% in ethanol. Working distance, voltage, and injection rate are consistent for all samples during electrospinning process. Smooth and straight nanofibers could be fabricated and observed from SEM for

composite samples. The diameter of nanofibers is < 200nm as seen in Fig 1b. The magnetization curves were obtained from SQUID measurement as shown in Fig.3. The paramagnetic property is found because the size of Fe₃O₄ nanoparticles is small (~10nm). The saturated magnetization for composite samples with 2.0 wt% and 3.8 wt% of DLF content is 1.15 and 2.15 memu/g respectively. The saturated magnetization of composite is proportional to the content of DLF.

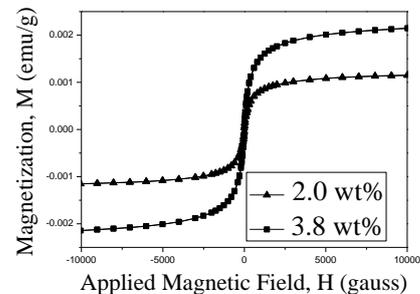


Fig.3 Magnetization curves with 2.0 wt% and 3.8 wt% of DLF content in composite

Conclusion

DLF/PNIPAAm composite samples were prepared. LCST was shifted from 32.4 to 31.5°C as the DLF content was larger than 2.6 wt%. Nanofibers of DLF/PNIPAAm with both thermo-responsive and magnetic properties were fabricated successfully via electrospinning process. The paramagnetic property is retained in the nanofibers.

Reference

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