Hindawi Publishing Corporation
Journal of Nanotechnology
Volume 2012, Article ID 138438, 5 pages
doi:10.1155/2012/138438

Research Article

Electrospun Polyvinylpyrrolidone-Based Nanocomposite Fibers Containing $(Ni_{0.6}Zn_{0.4})Fe_2O_4$

W. S. Khan,[1] R. Asmatulu,[1] Y. H. Lin,[2] Y. Y. Chen,[2] and J. C. Ho[2,3]

[1] *Department of Mechanical Engineering, Wichita State University, Wichita, KS 67260, USA*
[2] *Institute of Physics, Academia Sinica, Taipei 115, Taiwan*
[3] *Department of Physics, Wichita State University, Wichita, KS 67260, USA*

Correspondence should be addressed to R. Asmatulu, ramazan.asmatulu@wichita.edu and J. C. Ho, chienmingho@gmail.com

Received 9 March 2012; Accepted 10 April 2012

Academic Editor: Charles M. Lukehart

Polyvinylpyrrolidone-based nanocomposite fibers containing $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ have been successfully fabricated by an electrospinning technique. Magnetic measurements were made, individually, on polyvinylpyrrolidone, the ferrite nanoparticles, and several fibrous nanocomposites. The polymer exhibits a diamagnetic susceptibility comparable to the estimated value from Pascal's constants. The nanocomposites maintain intrinsic properties of pure $(Ni_{0.6}Zn_{0.4})Fe_2O_4$, with a weighted magnitude according to its concentration in a given fiber. Meanwhile, superparamagnetism prevails with a relatively low blocking temperature, assuring no aggregation of the fine particles. Such electrospun materials are flexible and have large surface area per unit mass, thus suitable for certain applications in environmental and biomedical engineering.

1. Introduction

Soft magnetic ferrites have been widely used in electronics because of their low cost and excellent performance. Recent research has been focused on fabricating nanoparticles and expanding their applications. For example, the lack of domain wall resonance makes single-domain ferrite nanoparticles suitable for high frequency compact-core devices [1], and polymeric microspheres containing ferrite nanoparticles for drug delivery [2] have been actively pursued with promising results.

This work was designed to fabricate electrospun fibers of polyvinylpyrrolidone (PVP) doped with mixed ferrite $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ nanoparticles and evaluate the product through magnetic characterization. Nanocomposite fibers have large surface area per unit mass and are highly flexible. Apart from magnetic storage and high-frequency antenna, their potential applications include environmental monitoring and filtration of small airborne contaminates [3] and, in the biomedical field, wound dressing, tissue engineering, as well as drug [4] and gene therapy [5].

Flexible one-dimensional microstructures can be produced by electrodepositing magnetic additives to porous membranes [6]. However, the method is not practical for oxides. Instead, Gupta et al. [7] have demonstrated successfully an electrospinning technique in producing submicron Estane fibers containing MnZnFe-Ni nanoparticles. Electrospinning is essentially a drawing process utilizing electrostatic force instead of mechanical and shearing forces in conventional fiber formation.

2. Experimental

2.1. Materials

2.1.1. Polyvinylpyrrolidone (PVP). PVP is a water-soluble polymer $(C_6H_9NO)_n$ made from the monomer *N*-vinylpyrrolidone (Figure 1). The Sigma Aldrich product used in this work has approximately 130,000 g/mol.

2.1.2. $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ Nanoparticles (MNP). Nano-scale $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ (herewith referred to as MNP) was used in this study. The composition was selected, because the 0.6/0.4 ratio for Ni/Zn corresponds to maximum saturation magnetization in the Ni-Zn mixed ferrite system [8, 9].

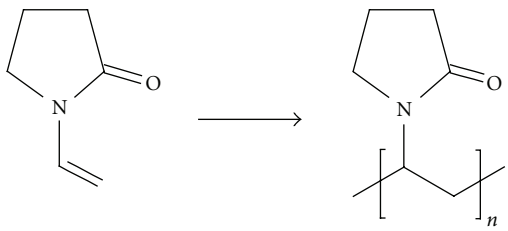

Figure 1: Polymerization of N-vinylpyrrolidone.

The materials were prepared by a coprecipitation process. Ni-, Zn-, and Fe-sulfates ($NiSO_4$, $ZnSO_4$, and $Fe_2(SO_4)_3$) from Sigma Aldrich were dissolved in deionized water, and heated up to 80°C with constant stirring at 700 rpm for 2-3 h. Following the drop-wise addition of NaOH, ferrite particles were produced and collected. Repeated washing removed all sulfate residues. Atomic force micrograph (Asylum Research, MFP-3D) in Figure 2 yields particle size of approximately 30 nm.

2.2. Nanocomposite Fibers by Electrospinning. Three samples were prepared, each having a nominal composition $x = 2$, 4, or 8, which refers to the weight percentage of MNP in the nanocomposite fibers.

The diagram in Figure 3 illustrates the setup for electrospinning process, which creates fine fibers through an electrically charged jet of PVP in ethanol containing ferrite nanoparticles. The polymeric solution is first transferred to a 10 mL syringe, which is connected to a capillary needle with an inside diameter of 0.5 mm. By immersing a platinum electrode in the solution, a DC power supply produces 10–30 kV against a grounded collector screen. With the syringe pump set at 2.5 mL/hr, the electric force overcomes the surface tension of the solution at the capillary tip, and a jet emerges. After travelling 1-2 cm, it follows a spiral pattern due to bending instability [10]. This looping motion makes the jet to stretch significantly before arriving at the collector screen placed at 25 cm away, during which part of the solvent evaporated. Residual solvent was removed afterward by drying the resulting fibers in an oven at 60°C for 8 h. Figure 4 shows the scanning electron microscopic image of typical electrospun nanocomposite fibers.

2.3. Magnetic Evaluations. The study addresses two basic questions: first, is the magnetic behavior of the composite fiber dominated by the nanoparticle inclusions? Secondly, do the nanoparticles maintain their magnetic properties in the fiber fabrication? Answer to the first question hinges on the relative magnetization between the polymer matrix and the relatively small amount, by weight, of $(Ni_{0.6}Zn_{0.4})Fe_2O_4$. To the second question, one needs to compare the magnetic behavior of the nanocomposite fibers to the expected values weighed by the intrinsic properties of parent $(Ni_{0.6}Zn_{0.4})Fe_2O_4$. Towards these ends, experimental data presented below are sequentially for PVP, $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ nanoparticles, and composite fibers containing MNP with $x = 2$, 4 and 8.

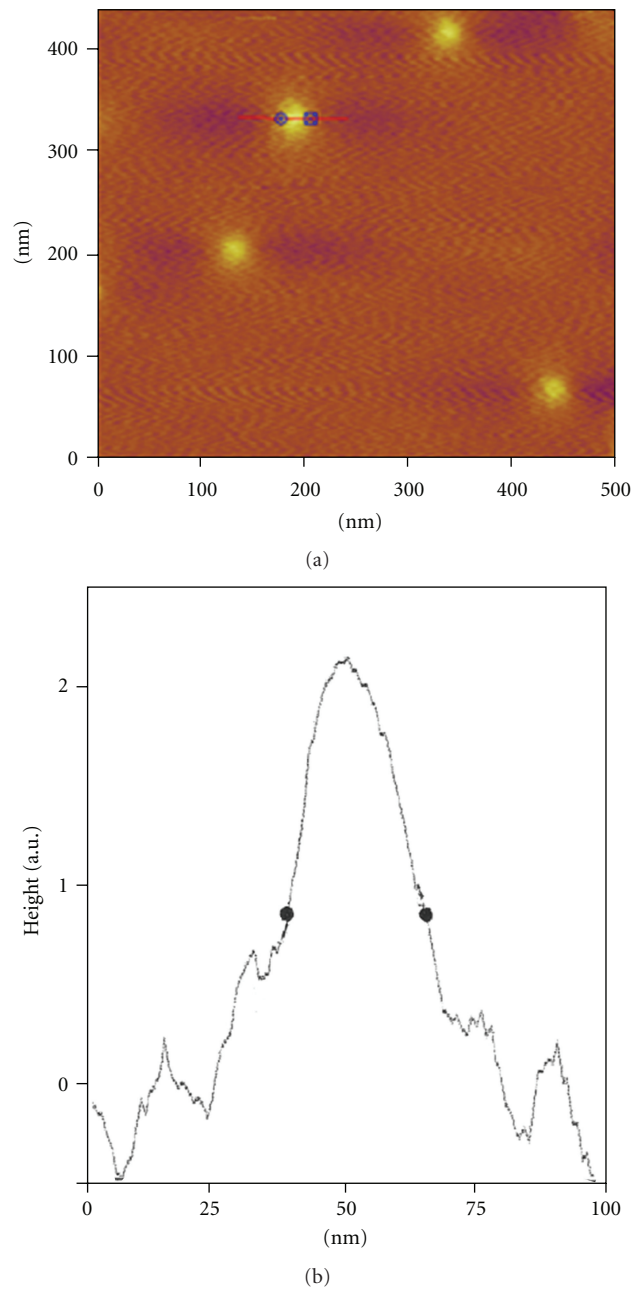

Figure 2: Atomic force micrograph reveals particles (a) of approximately 30 nm in size from scanning trace (b).

Magnetization measurements were made with a superconducting quantum interference device (SQUID). Each sample was characterized in terms of its magnetization at 300 K, but changing fields between +20,000 and −20,000 Oe.

For composite fibers with $x = 8$, another set of data was taken, in terms of temperature dependence of magnetization between 4 and 300 K. The measuring field of 100 G was applied after cooling to 4 K (i.e., zero-field-cooling or ZFC) or prior to cooling (i.e., field-cooling or FC). Comparison between the two sets of magnetization data could reveal the superparamagnetic nature of magnetic nanoparticles.

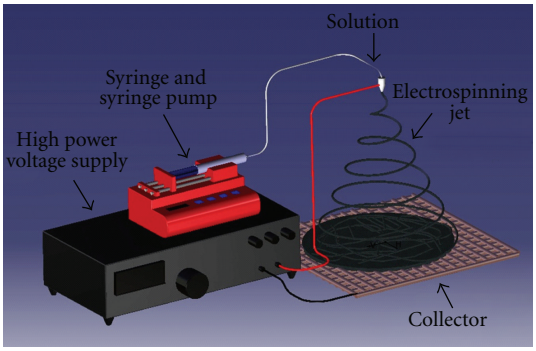

Figure 3: Diagram of electrospinning process.

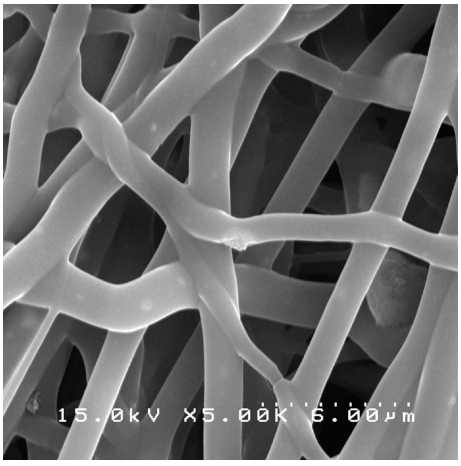

Figure 4: Electrospun fibers of PVP containing magnetic nanoparticles.

3. Results and Discussion

3.1. Polyvinylpyrrolidone (PVP). As the matrix and the major ingredient, in weight, of the composite, PVP's intrinsic magnetic behavior needs to be known. For polymers, the expected diamagnetism should yield a negative diamagnetization M_d linear with the external field. Accordingly, experimentally obtained magnetization M data in Figure 5 are fitted to two components. Apart from the diamagnetic $M_d = -0.742 \times 10^{-6} H$, another component $M_m = M - M_d$ shows saturation below 1,000 Oe. It likely arises from minor magnetic impurities in the industrial product. Nevertheless, it is negligible in data analysis below for MNP-containing samples, due to their orders-of-magnitude difference in M.

It has been suggested that diamagnetic susceptibility ($\chi_d = M_d/H$) of a particular compound can be calculated by

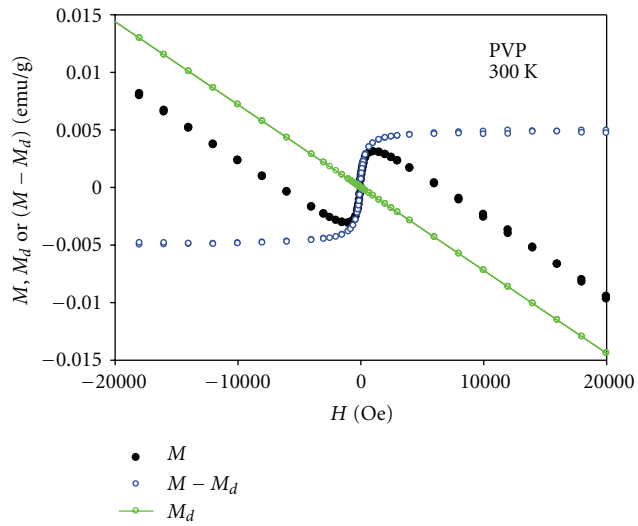

Figure 5: Magnetization M of PVP can be resolved into two components. The expected diamagnetic M_d is linearly proportional to H with a negative slope. The difference $(M - M_d)$, reaching saturation below 1,000 Oe, likely arises from minor magnetic impurities.

adding its individual atomic susceptibility or Pascal's constant, supplemented by constitutive corrections [11]. For the base unit of PVP (C_6H_9NO, 111 g/g-atom) having 6 C, 9 H, 1 O, and 1 N (in ring), including 4 C in ring and one double bond, the estimated diamagnetic susceptibility would be

$$\begin{aligned}\chi_d &= [6(-6.00) + 9(-2.93) + (-4.61) + (-4.61)] \\ &\quad + [4(-0.24) + (+5.5)] \\ &= [-71.6] + [+4.5] \\ &= -67.1(10^{-6}/\text{g-atom}),\end{aligned} \tag{1}$$

or -0.605×10^{-6}/g. This is fairly close to the experimentally obtained value of -0.742×10^{-6}/g, considering the simple assumptions in the Pascal's constants approach.

3.2. $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ Nanoparticles. Figure 6 exhibits the typical field dependence of magnetization for soft magnetic ferrites at 300 K. Saturation occurs near 2,500 Oe. The slow and nearly linear increase of magnetization at higher fields is often observed in fine particles, presumably due to surface moments.

While the saturation magnetization is almost twice as large for bulk materials [8, 9], the result here is in agreement with that reported earlier for nanoparticles [1]. The difference could be due to variation in cations distribution in the spinel structure, as well as the surface effect.

3.3. PVP-Base Fibers Containing Magnetic Nanoparticles. Figure 7 shows the field dependence of magnetization at 300 K for electrospun PVP-based nanocomposite fibers containing different amount of $(Ni_{0.6}Zn_{0.4})Fe_2O_4$. The general features are similar to that for pure $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ nanoparticles in Figure 6. Saturation prevails near 2,500 Oe in all curves. The 20,000-Oe data are in reasonable agreement

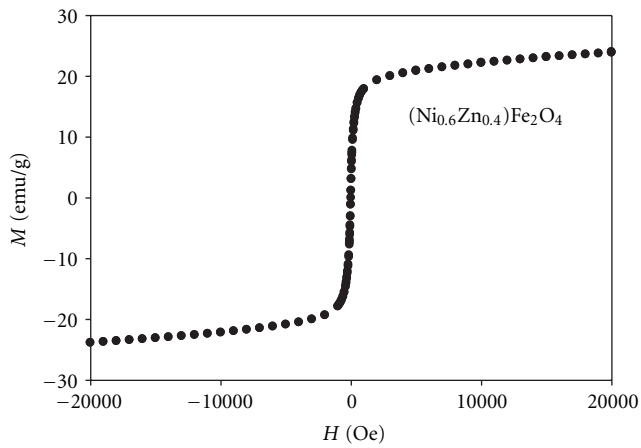

Figure 6: Magnetization of $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ nanoparticles at 300 K, reaching saturation near 2,000 Oe.

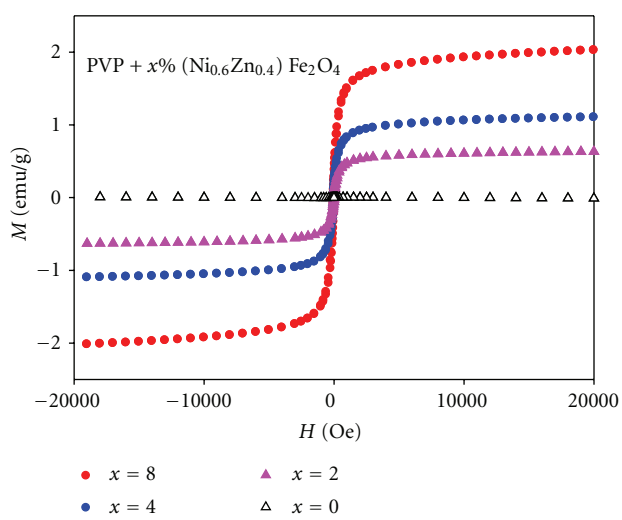

Figure 7: Field dependence of magnetization for PVP-based nanocomposite fibers.

with the weighted values for $x = 2$, 4 or 8. Small discrepancies are somewhat expected, considering that each sample for SQUID measurement had mass of only approximately 50 mg. Such a small sampling could easily reflect the lack of perfect uniformity of the particles distribution in the fiber. Nevertheless, it can be stated that the particles in the electrospun fiber well maintain their original magnetic characteristics.

The sample with $x = 8$ was used for a superparamagnetic evaluation. Basically, ferrites become ferrimagnetically ordered below a Curie temperature, which is much higher then 300 K. However, each nanoparticle has a single domain, unless aggregation occurs, and its tendency to align with the applied field has exponential slow rates at low temperatures due to anisotropic barriers. In the case of ZFC, the initially random particles alignment yields a low magnetization at 4 K as observed. After a measuring field is applied,

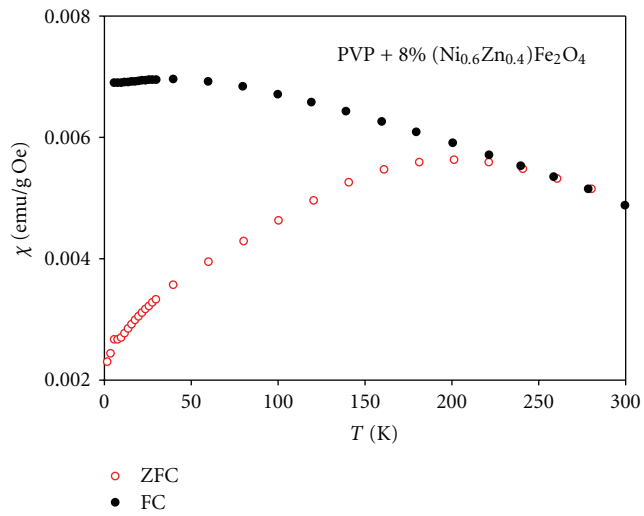

Figure 8: Temperature dependence of magnetic susceptibility at 100 Oe for zero-field-cooled and field-cooled PVP + 8% MNP, showing a blocking temperature near 250 K.

the magnetization rises with increasing temperature and approaches equilibrium value as revealed by the FC.

Indeed, a superparamagnetic behavior for $x = 8$ prevails in Figure 8. At 100 Oe, the ZFC and FC curves merge at a blocking temperature T_B near 250 K. The observation provides confirmation of a well-dispersed distribution of MNP in the fiber.

4. Conclusions

Polyvinylpyrrolidone-based fibers containing $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ nanoparticles have been successfully fabricated by an electrospinning technique. Magnetic measurements on polyvinylpyrrolidone reveal an expected diamagnetic behavior and a small magnetic contribution presumably from minor impurities. Both terms are negligibly small. The nanocomposites maintain intrinsic properties of $(Ni_{0.6}Zn_{0.4})Fe_2O_4$, with a weighted magnitude according to its concentration in a given fiber. Meanwhile, superparamagnetism prevails with a relatively low blocking temperature, assuring no aggregation of the fine particles. Such electrospun materials are flexible and have large surface area per unit mass, thus suitable for certain applications in environmental and biomedical engineering.

Acknowledgment

Work at Academia Sinica was under Grant NSC 97-2120-M-001-007 of National Research Council, China.

References

[1] B. P. Rao, A. M. Kumar, K. H. Rao et al., "Synthesis and magnetic studies of Ni-Zn ferrite nanoparticles," *Journal of Optoelectronics and Advanced Materials*, vol. 8, no. 5, pp. 1703–1705, 2006.

[2] R. Asmatulu, A. Fakhari, H. L. Wamocha et al., "Drug-carrying magnetic nanocomposite particles for potential drug delivery systems," *Journal of Nanotechnology*, vol. 2009, Article ID 238536, 6 pages, 2009.

[3] H. W. Li, C. Y. Wu, F. Tepper, J. H. Lee, and C. N. Lee, "Removal and retention of viral aerosols by a novel alumina nanofiber filter," *Journal of Aerosol Science*, vol. 40, no. 1, pp. 65–71, 2009.

[4] D. G. Yu, L. M. Zhu, K. White, and C. Branford-White, "Electrospun nanofiber-based drug delivery systems," *Heath*, vol. 1, no. 2, pp. 67–75, 2009.

[5] A. Saraf, L. S. Baggett, R. M. Raphael, F. K. Kasper, and A. G. Mikos, "Regulated non-viral gene delivery from coaxial electrospun fiber mesh scaffolds," *Journal of Controlled Release*, vol. 143, no. 1, pp. 95–103, 2010.

[6] A. Fert and L. Piraux, "Magnetic nanowires," *Journal of Magnetism and Magnetic Materials*, vol. 200, no. 1–3, pp. 338–358, 1999.

[7] P. Gupta, R. Asmatulu, R. Claus, and G. Wilkes, "Superparamagnetic flexible substrates based on submicron electrospun estane® fibers containing MnZnFe-Ni nanoparticles," *Journal of Applied Polymer Science*, vol. 100, no. 6, pp. 4935–4942, 2006.

[8] C. Caizer, M. Stefanescu, C. Muntean, and I. Hrianca, "Studies and magnetic properties of Ni-Zn ferrite synthesized from the glyoxilates complex combination," *Journal of Optoelectronics and Advanced Materials*, vol. 3, no. 4, pp. 919–924, 2001.

[9] P. Yadoji, R. Peelamedu, D. Agrawal, and R. Roy, "Microwave sintering of Ni-Zn ferrites: comparison with conventional sintering," *Materials Science and Engineering B*, vol. 98, no. 3, pp. 269–278, 2003.

[10] D. H. Reneker, A. L. Yarin, H. Fong, and S. Koombhongse, "Bending instability of electrically charged liquid jets of polymer solutions in electrospinning," *Journal of Applied Physics*, vol. 87, no. 9, pp. 4531–4547, 2000.

[11] A. Earnshaw, *Introduction to Magnetochemistry*, Academic Press, New York, NY, USA, 1968.