

Preparation of Magnetic Poly(vinyl alcohol) (PVA) Materials by *In Situ* Synthesis of Magnetite in a PVA Matrix

Hai Lin,¹ Yoshimi Watanabe,² Mutsumi Kimura,¹ Kenji Hanabusa,¹ Hirofusa Shirai¹

¹Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda 386-8567, Japan

²Department of Functional Machinery and Mechanics, Faculty of Textile Science and Technology, Shinshu University, Ueda 386-8567, Japan

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ABSTRACT: An easy method for manufacturing homogeneous inorganic–organic materials, especially composite fibers, was obtained by the *in situ* synthesis of inorganic particles within polymer matrices. In this article, nanosized magnetite particles were synthesized *in situ* within poly(vinyl alcohol) (PVA) solutions by precipitating Fe²⁺ ions or a mixture of Fe²⁺ and Fe³⁺ ions with NaOH solution. As a result, magnetite particles with an average diameter of 20 nm were obtained homogeneously within the solutions because of the tridimensional structure and chelating capacities of PVA. Transparent films were obtained by a casting method, and six kinds of magnetic PVA fibers were also

prepared by a wet-spinning method from the solutions containing magnetite nanoparticles. The mechanical properties and the saturation magnetization of the fibers were measured. These fibers, which contain iron ions with a maximum content of 17.63 wt %, can be successfully fabricated by the *in situ* synthesis and they exhibit excellent magnetization properties (i.e., the largest saturation magnetization is 13.38 emu/g). © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1239–1247, 2003

Key words: composites; nanotechnology; particle size distribution; *in situ* synthesis; magnetic fiber

INTRODUCTION

One of the useful magnetic materials may be magnetic fiber. Magnetic fibers are used for applications such as magnetic paper, health-care cloth, magnetic filters, electromagnetic wave adsorbents, and various other application because of their high forming abilities. Preparation of magnetic fibers has been reported by coating magnetite particles on the surface of pulp,¹ cellulosic fibers,² and spider silk.³ In the aforementioned papers, the losses of mechanical properties were diminished, however, the magnetization of these fibers was not high enough for magnetic application because very small amounts of magnetite particles were adsorbed on only the surface of the fibers. To obtain a magnetic fiber with higher magnetization, we consider that it should be realized by spinning a polymer solution containing magnetic particles into fibers directly. Nevertheless, because of the large size and assembly of the available commercial magnetic particles, it is still difficult to obtain a continuous spinning process from such a spinning solution. Moreover, it is also difficult to keep the mechanical properties during

the complicated preparation process. Therefore, further endeavors seem to be necessary to disperse homogeneous magnetic particles with smaller size into a spinning solution.

Recently, nanosized magnetic materials have gained increasing interest because of the development of nanotechnology.^{4–14} Among these nanotechnology studies, polymer-blended magnetic materials are now extensively studied because of their high process ability, versatility, and lower cost.^{6a–10} However, there is indeed a major difficulty in obtaining well-characterized materials because of the assembly of the particles. Meanwhile, polymers with a tridimensional structure, especially chelating resins, such as derivatives of polystyrene,¹¹ poly(vinyl pyridine),¹² polyimine,¹³ and poly(vinyl acetate),¹⁴ have rigid pores that set upper limited inside growth space to the particles. One convincing reason for the formation of the tridimensional structure is the crosslinking reactions formed by coordinate bonds between the polymers and metal ions contained in particles. By this *in situ* synthesis of inorganic particles within polymer matrices, homogeneous inorganic–organic materials can be obtained easily. Among chelating resins, poly(vinyl alcohol) (PVA) has lately drawn considerable attention because of its capabilities of chelating hydroxyl groups to retain metal ions and hydrogen bonds leading to a tridimensional structure. Although there are several pa-

Correspondence to: H. Shirai (hshirai@giptc.shinshu.ac.jp).

TABLE I
Mechanical Properties of Magnetic Fibers

Sort	Fiber	Fe ²⁺ /PVA (mol%)	Fe ³⁺ /PVA (mol%)	Fineness as Denier (g/9000 m)	Young's Modulus (GPa)	Strength (MPa)	Elongation (%)
1	1	10	0	32	1.83 ± 0.40	47.4 ± 0.2	51.0 ± 0.5
1	2	20	0	34	1.69 ± 0.30	22.7 ± 0.3	48.6 ± 0.7
1	3	30	0	32	1.79 ± 0.30	29.3 ± 0.3	54.2 ± 0.5
2	4	5	5	34	1.91 ± 0.30	35.3 ± 0.3	51.9 ± 0.5
2	5	10	10	36	1.54 ± 0.20	23.2 ± 0.2	43.2 ± 0.4
2	6	15	15	34	1.21 ± 0.40	14.8 ± 0.3	32.8 ± 0.3

pers on magnetic PVA materials,^{15–18} none of them refer to *in situ* synthesis of magnetic particles within a PVA matrix nor report preparation of magnetic PVA fibers.

Magnetite (Fe₃O₄) is a famous magnetic material. Among the publications on magnetite nanoparticles,^{6,11,12,14} only a few refer to the controlling process of particle size within a polymer matrix by *in situ* synthesis. *In situ* synthesis has the potential to control the mean particle size and size dispersion of the nanoparticle population. A further possibility might be to modify magnetic films and fibers by filling polymers that have high forming abilities with magnetite nanoparticles. Success in nanometric size control and homogeneous dispersion of particles easily leads to an easy preparation of magnetic materials with fine characteristics.

Hence, in this article, we have tried to discuss a new method for preparation of organic–inorganic materials, especially composite fibers. The composites were prepared by *in situ* synthesis of inorganic nanoparticles within polymer matrices. Concretely, we have attempted to prepare magnetite nanoparticles *in situ* within PVA solutions. From the homogenous dispersed solutions, magnetic films and fibers were obtained very easily by a casting and a wet-spinning method, respectively. The synthesis and size controlling of magnetite nanoparticles are discussed. The preparation of the spinning solutions, the spinning method, the mechanical properties, and the magnetization of the fibers were studied in detail.

EXPERIMENTAL

Materials

PVA powder (DP = 32,000; degree of saponification = 100%) was used. FeCl₂ · 4H₂O and FeCl₃ · 6H₂O were special grade reagents and the other chemicals were reagent grade from WAKO Pure Chemical. Inc.

In situ synthesis of magnetite nanoparticles within 1.0 M PVA solution

Sort 1

First, 10.0 mL of Fe²⁺ ion solution (1.0 M) was added to 100.0 mL of PVA solution (1.0 M, as the concentra-

tion of constitutional repeating unit) and stirred at 45°C until well distributed. A solution of 3.0 M NaOH was then dropped slowly into the mixed solutions with stirring at 60°C until a pH of 12.0 ± 0.2 was attained.

Sort 2

First, 5.0 mL of Fe²⁺ ion solution (1.0 M) and 5.0 mL of Fe³⁺ ion solution (1.0 M) were added into 100.0 mL of PVA solutions and then treated according to the same method as just described in Sort 1.

The solutions were allowed to stand at room temperature and then dialyzed with distilled water using a cellulose dialysis membrane (WAKO, SIZE 36) until neutrality was attained. The obtained solutions were made into films by a casting method.

Preparation of magnetite-filled PVA spinning solutions

Two sorts and six kinds of spinning solutions were prepared. In this article, six kinds of fibers are manufactured by using these spinning solutions. Notation of the six fibers is listed in Table I.

Sort 1

First 10.0 mL of Fe²⁺ ion solutions (6.0, 12.0, 18.0 M) were mixed into 150.0 mL of 4.0 M PVA solutions and stirred at 45°C until well distributed. A solution of 3.0 M NaOH was then dropped slowly into the mixed solutions under stirring at 60°C until pH 8.0 ± 0.2 was attained. The solutions were allowed to stand at room temperature and then dialyzed with distilled water with a cellulose dialysis membrane until neutrality was obtained.

Sort 2

First, 10.0 mL of Fe²⁺ solutions (3.0, 6.0, and 9.0 M) and 10.0 mL of Fe³⁺ solutions with same concentrations were added into 150.0 mL of 4.0 M PVA solutions. The mixed solutions were then treated by the same methods as already described for Sort 1.

The dialyzed solutions were concentrated to the initial volume with a vacuum evaporator (TOKYO RIKAKIKAI, EYELA) at 45°C. The concentrated solutions were then filtered with a glass filter (SIBATA, 17GP250) and used as spinning solutions after de-airing.

Wet-spinning

A wet-spinning apparatus utilizing an immersion method (MUSASINO, KS-18525) was used in this experiment. The spinning solutions were maintained in an autograve at 45°C and pulled into a coagulation bath through a nozzle (one hole, 0.5 mm in diameter) by an air pump and a gear pump at a flow speed of 0.3 mL/min. A 400-g/L solution of Na₂SO₄ was used as a coagulation solution. The filament from the spinneret was drawn through a coagulating bath (2.0 m in length) and dried on a set of rollers (0.20 m in diameter). The dried fibers were then wound on a bobbin at a speed of 44 ± 2 m/min. The fibers were washed with a mixed solution of water and methanol (50:50), and methanol, and finally dried at 40°C under vacuum.

Characterizations of the fibers

The photographs of the fibers were taken with a scanning electron microscope (SEM; HITACHI, S-2380). The size of magnetite particles was observed with a transmission electron microscope (TEM; JEOL, JEM-2010). The solutions were diluted 10 times with water and dropped on a copper grid coated with a carbon film.

Tensile tests were carried out according to JIS L1013 for the testing method of tensile properties of the fibers. Ten fibers (each of 40 mm length) from each sample were tested and their averages were compared. All fibers were conditioned at 20 ± 2°C and 65 ± 2% relative humidity for 24 h in a controlled environment room before measuring the tensile properties with an autograph (SHIMAZU, AG-20KND). The full-scale load was 1.0 g and the strain speed was 20 mm/min.

After hydrolyzing the fibers with H₂SO₄ and HClO₄ solutions, the contents of iron ions within the fibers were measured by atomic absorption spectrometry (AAS; HITACHI, 180-50). The thermogravimetric analysis of the fibers was determined with a TG-DTA tester (SEIKO, TG-DTA220) at a heating rate of 15°C/min under air. All runs were carried out with a sample of 2.0–5.0 mg. The crystal structure analysis was carried out using CuKα in an X-ray tester (RIGAKU, 2001) at a range of 3 to 60°. The magnetism of the fibers was measured with a vibrating sample magnetometer (RIKEN DENSHI, BHV-55) at room temperature.

RESULTS AND DISCUSSION

In situ synthesis of magnetite

It is well known that magnetite crystals have an inverse spinel structure. It is also well known that magnetite is formed by Fe²⁺ and Fe³⁺ ions with a molar ratio of 1:2.¹⁹ Oxidizing Fe²⁺ ions (Sort 1) or Fe²⁺/Fe³⁺ ions (mixture of Fe²⁺ and Fe³⁺ ions, Sort 2) with alkaline solutions under air can prepare magnetite. In the previous studies, the preparation of magnetite has been reported from Fe²⁺/Fe³⁺ mixtures with molar ratios of 1:2^{20–22} or 1:1.²² However, because Fe²⁺ ions can be oxidized easily by ambient oxygen in air^{21, 23–24} or in PVA during stirring in PVA solutions, we have tried to prepare the magnetite from Fe²⁺/Fe³⁺ ions with a mole ratio of 1:1 and also from Fe²⁺ ions singly within a PVA matrix.

First, we would like to discuss the synthesis of magnetite from Fe²⁺ ions within the PVA matrices (Sort 1). Before the addition of NaOH solution, PVA adsorbed Fe²⁺ ions homogeneously because of the chelating reaction between hydroxyl groups and Fe²⁺ ions during the mixing process. The adsorption was followed visually by observing color changes from white through green and finally to orange-red under air. The orange-red color indicated that some of Fe²⁺ ions were oxidized to Fe³⁺ ions in the presence of PVA, presumably by residual oxygen in air or the hydroxides of PVA. This preoxidation under air is an important factor affecting the final component of iron oxide in the following step. The addition of NaOH solution into the mixed solution resulted in slow color changes from orange-red through brown, and finally to black. Here, the brown color could be considered as the color of maghemite (γ-Fe₂O₃)²² as an intermediate and the black as the formation of magnetite.

During the *in situ* synthesis, the tridimensional structure of the PVA matrix provides a limited formation space for magnetite to control the size and also prevents the assembly of particles. By controlling the pH value of the solution, we obtained magnetite nanoparticles with different sizes. The TEM images of magnetite nanoparticles in the solution at different pH values are shown in Figure 1. It is seen from these photographs that the size of nanoparticles increases with the addition of NaOH solution, and exhibits homogeneous size at those pH values. The nanoparticles show average diameters of 2.0 nm at pH 3.37, 4.0 nm at pH 4.23, and 8.0 nm at pH 6.72. At pH >8.0, the growth of particles stopped, and the nanoparticles began to self-assemble. In this experiment, because the tridimensional structure of PVA sets an upper limit to the growth of the nanoparticles, the growth was limited at a final size of ~20 nm, and the particles showed an even dispersion. We can observe that the nanoparticles showed almost the same size even in the pH range 8.16–12.01.

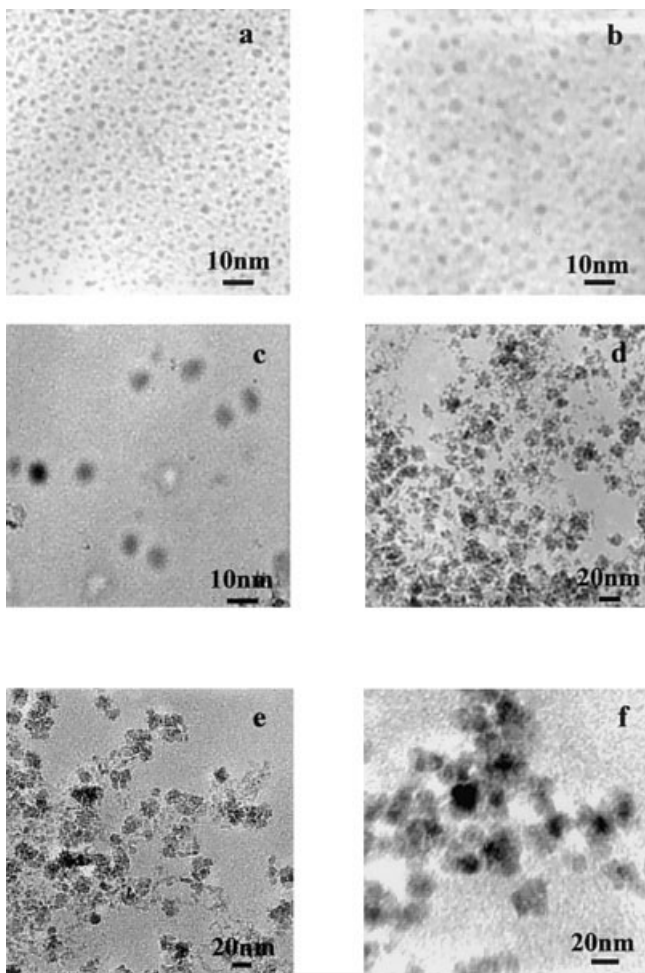


Figure 1 TEM images of magnetite nanoparticles synthesized *in situ* within a 1.0 M PVA solution at (a) pH 3.37, (b) pH 4.23, (c) pH 6.72, (d) pH 8.16, (e) pH 10.28, and (f) pH 12.01.

We have dealt with the Sort 1, in which the oxidation of Fe^{2+} to Fe^{3+} is a most important reaction and the final yield of magnetite is influenced by this reaction. However, it is difficult to control the oxidation of Fe^{2+} to Fe^{3+} during the processes of Sort 1. Next, let us discuss the synthesis of magnetite from mixtures of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions within the PVA matrices (Sort 2). In the case of the solutions of Sort 2, the color change was from white to orange-red during the adsorption process. In this case, the filling sequence of the iron ions was very important. It seems more difficult to synthesize magnetite by first filling with Fe^{3+} , and easier by filling with Fe^{2+} and Fe^{3+} ions at the same time than by filling with Fe^{2+} ions first. The adsorption of iron ions into PVA possibly affects the size and the content retention of magnetite in the following processes. On the other hand, more precipitation of solutions appeared in Sort 2 because of a quicker reaction between iron ions and NaOH than in Sort 1. During the addition of NaOH solution, the synthesis in Sort 2 shows a similar phenomena to that shown in Sort 1.

Factors influencing the synthesis

Hitherto, the *in situ* syntheses were performed under air atmosphere. To discuss the influence of ambient oxygen, the *in situ* syntheses of magnetite nanoparticles within PVA solutions was also studied under a nitrogen atmosphere. After Fe^{2+} ions were added into PVA solution, the color of this solution changed from green to orange-red after stirring both under air and nitrogen atmosphere, presumably because little Fe^{2+} was oxidized to Fe^{3+} by the oxidation in PVA, even under nitrogen atmosphere. With the addition of NaOH, the colors of solutions changed from orange-red through brown to black under air, and from orange-red to brown under nitrogen atmosphere. Moreover, for a same final pH value of the two solutions at 8.0 ± 0.2 , almost the same volumes of NaOH solution were added respectively. This result indicates that not only NaOH but also oxygen are important to synthesize magnetite; nevertheless, the influence of oxygen in air on the synthesis of magnetite is still unclear.

The X-ray diffraction patterns of the obtained films, which were manufactured under air or nitrogen atmosphere, are shown in Figure 2. The results show that the films obtained from Sort 2 under air or nitrogen and from Sort 1 under air display the same sharp reflections assigned to the magnetic components. It should be noted, however, that only a peak assigned to the reflection of PVA appeared in the film obtained

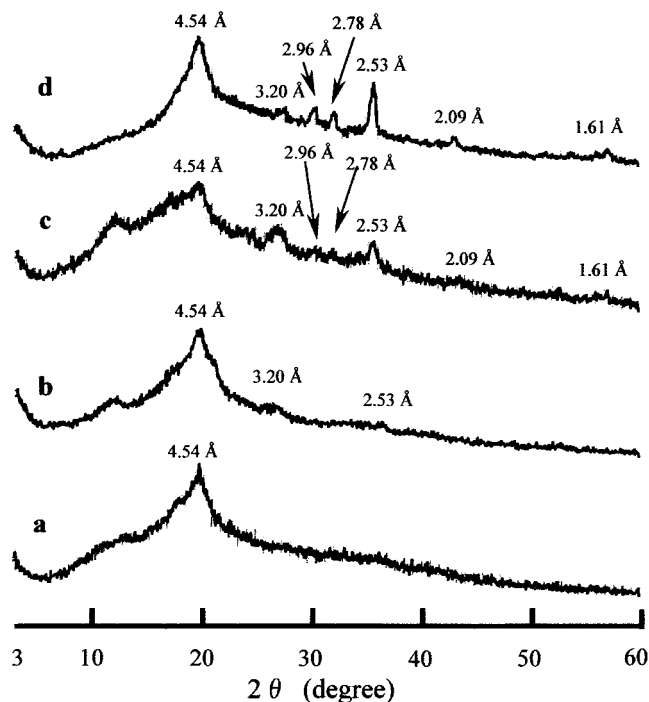


Figure 2 X-ray diffraction patterns of PVA films prepared from Fe^{2+} under (a) a nitrogen atmosphere and (b) an air atmosphere, and from $\text{Fe}^{2+}/\text{Fe}^{3+}$ under (c) a nitrogen atmosphere.

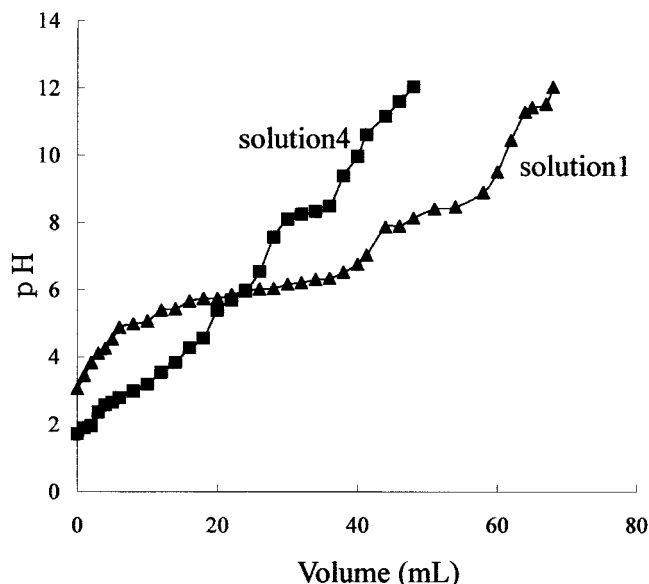


Figure 3 The pH changes in spinning solutions 1 and 4 with the addition of NaOH solution.

from Sort 1 under nitrogen. Therefore, we can conclude that preoxidization of Fe^{2+} ions to Fe^{3+} ions by ambient oxygen in air is a necessary condition to prepare magnetite in Sort 1. All the obtained films are transparent because of the small size and the even dispersion of particles.

After the NaOH solution was added, the pH value of these solutions increased quickly during the first 1 min. With further stirring, the pH value decreased slowly and stabilized after 20 min. The NaOH–pH curves of the spinning solution 1 (Sort 1) and 4 (Sort 2) are shown in Figure 3. These curves indicate the variation of pH value of solutions achieved by the addition of NaOH solution. As compared with Sort 2, less of NaOH solution was added in Sort 1, and presumably the oxidization of Fe^{2+} ion to Fe^{3+} ions consumed a part of NaOH solution. The exponential increase in speed of Sort 2 was also quicker than that of Sort 1. Those data indicate that the formation of magnetite was easier in Sort 2 than in Sort 1. On the other hand, we can observe a similar tendency from both Sort 1 and Sort 2 that the curves show steep rises around pH 8.0 (pH 7.5–8.5). It can be considered that under pH 8.0, the addition of NaOH contributed greatly to the growth of magnetite. The growth showed stability around pH 8.0. This result agrees with the observation by TEM. The further addition of NaOH solution precipitated PVA solutions in quantity; therefore, the pH value was remained around pH 8.0 for a while. After that, the final addition of NaOH solution increased the pH value marginally.

Although the synthesis of magnetite can occur spontaneously at room temperature,^{21, 22} in this experiment, the synthesis was conducted at 60°C in view of

the solubility of PVA. The initial addition of NaOH solution led to a black precipitate instantly, and the precipitate dissolved slowly again with stirring at 60°C. The further addition of NaOH solution would also lead to precipitate if the stirring speed was slower than 400 rpm. With the dissolution of the precipitate, the color of the solutions changed from orange-red through brown and to black at last.

During the dialysis process, no color change appeared in distilled water out of the cellulose dialysis membrane. Furthermore, no iron ions were observed within the used water as determined by AAS. It can be considered that all the iron ions were adsorbed by PVA with strong chelate bonds or formed particles. Using a glass filter, precipitate of PVA and magnetite with a large size were removed. The precipitates were formed because of the crosslinking of PVA and assembly of magnetite.

Wet-spinning

PVA is one of most important synthesis polymers used in the textile industry today. It can be spun into fibers by wet-spinning methods: solution spinning and gel-spinning. In this experiment, we have used the solution spinning method and Na_2SO_4 solution as a coagulant. Two factors are remarkable for obtaining a fine spinning solution: the initial concentration of PVA solution and the final pH value of the mixture. When the initial concentration of PVA solutions is >4.0 M, PVA promptly precipitates rapidly in quantity with the addition of NaOH solution. On the other hand, the *in situ* synthesis of magnetite needs a high pH value, but the high pH value also leads to a coagulation of PVA. Both a high concentration of PVA solution and a high pH value will lead a decrease in the content of magnetite in the fibers after filtering. A PVA solution with a concentration of 4.0 M and a final pH value of 8.0 ± 0.2 is suitable for obtaining fine spinning solutions.

With a wet-spinning method, we succeeded in preparing six kinds of magnetic fibers: fibers 1 to 3 belong to Sort 1 and fibers 4 to 6 belong to Sort 2 (Table I). It must be emphasized here that this method is easy to perform with a continuous process. The SEM images of the random magnetic fibers with an average diameter of 50–80 μm are shown in Figure 4. The fibers show a smooth surface, and there are no crystals on the surfaces (Figure 5). Two interesting phenomena are apparent; namely, fiber 1 shows a hollow structure and fiber 6 shows a porous structure, as shown in Figure 4. The hollow structure only appears in Sort 1 and disappears as the content of magnetite increases, as in fibers 2–6. In contrast, we found a porous structure in fiber 6. Further investigations on phase separations during the spinning process are necessary to

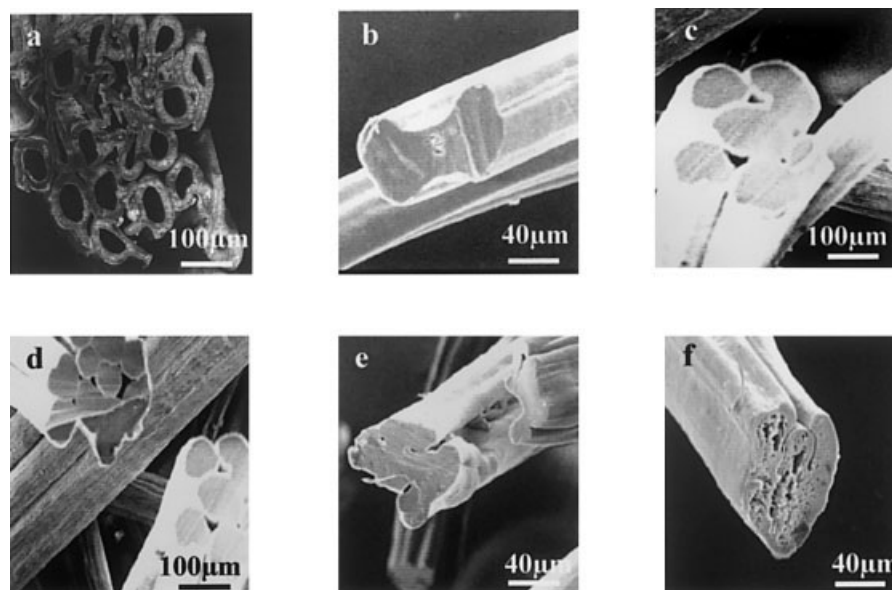


Figure 4 SEM cross-section images of fibers 1–6: (a) fiber 1; (b) fiber 2; (c) fiber 3; (d) fiber 4; (e) fiber 5; and (f) fiber 6.

understand the formation mechanism of the hollow and porous structures in fibers.

After dissolving the fibers in water (4.0 g/L), we observed the TEM images of magnetite nanoparticles within fibers 1–6, which are shown in Figure 6. As can be seen, the final sizes of magnetite particles were almost same and the average diameter was 20 nm, although the content of magnetite in each fiber is different. We have determined the particles size distribution in each sample from >400 particles in three different TEM images (not shown). This analysis shows that in each sample, the particles with a mean diameter of 20.0 ± 0.5 nm have the highest distribution and all are >60% (Figure 7). In comparison to 50–80 μm fibers, the magnetite particles are small enough, and we succeeded in obtaining a continuous spinning process because of the homogeneous dispersion of magnetite nanoparticles within the spinning solutions.

The mechanical properties of the fibers are very important considerations for many applications. Generally, by controlling the shrinkage and elongation rate at least at two stages after washing and during

drying, a fiber with good mechanical properties can be obtained. In this experiment, the apparatus used has no elongation machine and washing bath, and we did

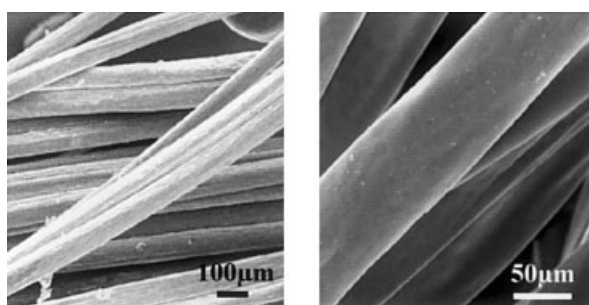


Figure 5 SEM surface images of fiber 4.

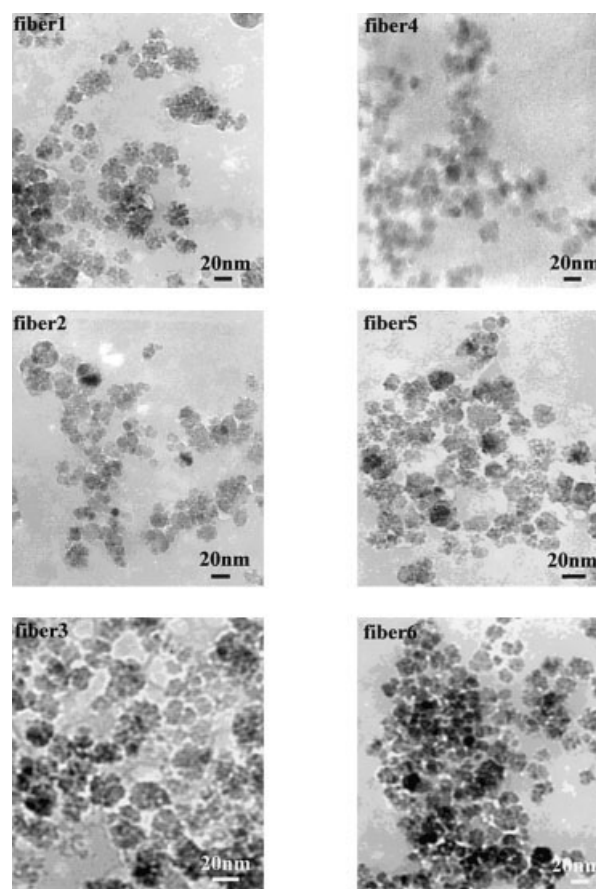


Figure 6 TEM images of magnetite nanoparticles within fibers 1–6.

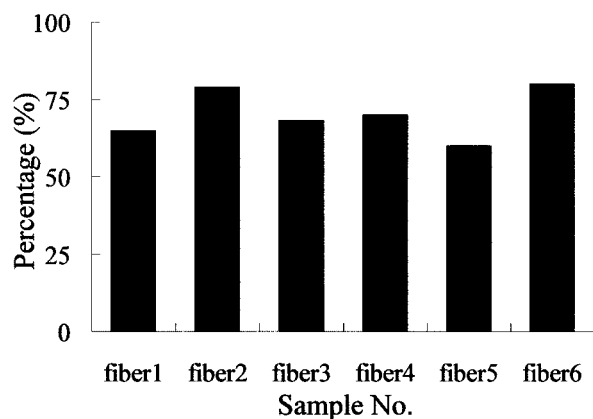


Figure 7 A histogram plot of particle size distribution, of particles with a mean diameter of 20.0 ± 0.5 nm, within the fibers (based on TEM).

not expose the fiber to any further drawing treatment. As a result, the obtained fibers exhibited Young's moduli of 1.20–2.00 GPa, breaking strengths of 14.0–48.0 MPa, and elongation of 32–55%. These mechanical properties of the fibers are also listed in Table I. The Young's modulus and breaking strength decreases with an increase of the magnetite content. On the other hand, the fibers show a similar elongation percentage of $\sim 50\%$, except for fiber 6. We have also tried to spin a PVA fiber under the same spinning conditions and the obtained a PVA fiber that exhibits mechanical properties with a Young's modulus of 5.84 ± 0.50 GPa, a breaking strength of 47.8 ± 0.4 MPa, and elongation of $94.0 \pm 0.3\%$. Compared with this pure PVA fiber, the obtained composite fibers exhibit few weak mechanical properties. However, better properties could be expected by using additional treatments such as drawing.

Content of magnetite within the fibers

The results of AAS and TGA are shown in Table II. The TGA data show the weight residues of fibers heated to 540°C under air. At 540°C , all iron ions should be oxidized to hematite ($\alpha\text{-Fe}_2\text{O}_3$) under air atmosphere. The TGA data were higher than the results of AAS after calculating the ratio of residues to iron ions. This result is possibly because the fibers contain plenty of Na_2SO_4 crystals and magnetite was oxidized to hematite by ambient oxygen in air atmosphere. The results of AAS show that the fibers contain

iron ions (both Fe^{2+} and Fe^{3+} ions), with high densities in a range 6.83–17.63 wt %. Note that the yields of iron oxides in fibers from Sort 2 are much larger than those in fibers from Sort 1 because the preoxidation in Sort 1 did not provide enough Fe^{3+} ions for the formation of magnetite under an air atmosphere alone. Moreover, the content of magnetite within the fibers is less than the added iron ions. Presumably, magnetite particles with large size were removed in a great quantity during the filtering process and not all of the irons could be precipitated to magnetite at the final pH value of 8.0 ± 0.2 . The differences of iron ions contents also lead to different colors of the fibers, for example red-brown in fiber 1 and black in fibers 2–6.

X-ray diffraction

The wide-angle X-ray diffraction (WAXD) patterns of the fibers are shown in Figure 8. PVA is a crystalline polymer and a WAXD pattern of PVA displays two sharp reflections at $d = 4.54$ and 3.20 Å.^{25, 26} The diffraction spacings for magnetite and maghemite ($\alpha\text{-Fe}_2\text{O}_3$) are similar,^{26, 27} and the peaks are too weak to be distinguished.^{21, 23, 24} In this paper, the obtained peaks are sharp enough and appear at $d = 2.96, 2.78, 2.64, 2.53, 2.32, 2.23, 2.09, 2.03,$ and 1.61 Å. These peaks closely resemble those assigned to the reflections of magnetite.^{26, 27} These remarks bear out a conclusion that magnetite is the final main formation of iron oxides. Not all of these peaks can be observed in both Sort 1 and Sort 2, and more peaks were observed in Sort 2 than in Sort 1.

Magnetism of the fiber

Magnetism is one of the most important properties of the magnetic fibers. Therefore, M – H curves (change of magnetization versus the magnetic field) of the fibers must be accurately measured. M – H curves are obtained by measuring the induced electromotive force generated by flux changes. A hysteresis curve as a function of the applied magnetic field obtained from fiber 3 is shown in Figure 9. Although data from other fibers are not presented here, they show the same tendency except for the absolute values. Saturation magnetization of each fiber can be evaluated from the M – H curve.

TABLE II
Results of AAS and TGA

Parameter	Fiber 1	Fiber 2	Fiber 3	Fiber 4	Fiber 5	Fiber 6
Iron ion/fiber (wt %, AAS)	6.83	8.93	11.23	9.41	15.23	17.63
Weight residue (wt %, TGA) ^a	13.36	20.27	24.27	21.39	26.07	29.11

^a The fibers were heated to 540°C under air.

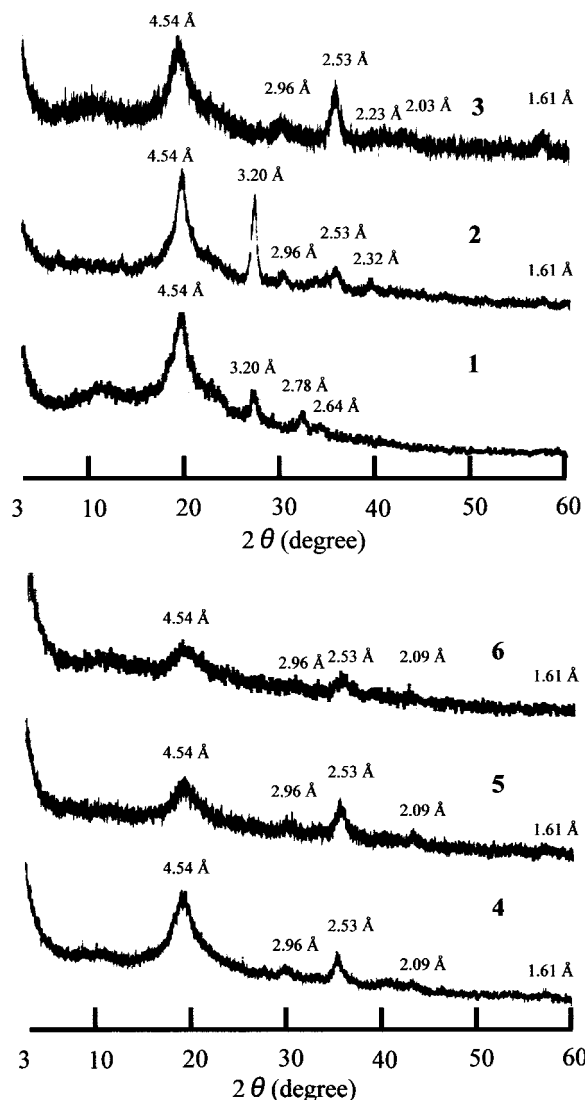


Figure 8 X-ray diffraction patterns of fibers 1-6.

The relationship between saturation magnetization and concentration of filled iron ions (primary iron ion concentration of spinning solution) is shown in Figure

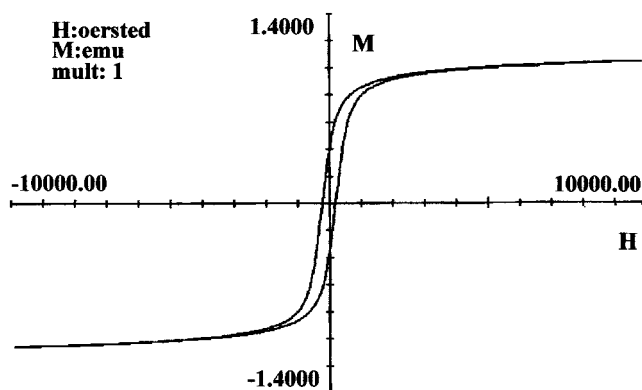


Figure 9 Plot of the applied magnetic field (H) versus magnetization (M /emu) for 0.085 g of fiber 3, showing hysteresis at room temperature.

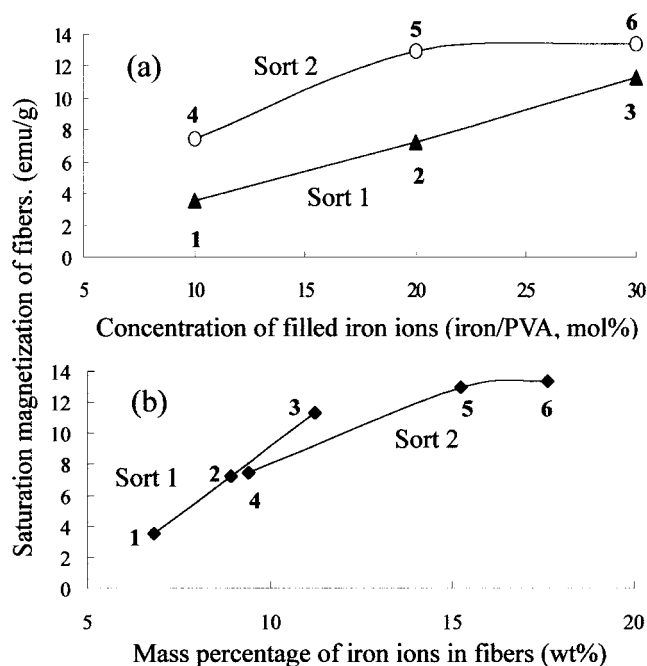


Figure 10 Change in the saturation magnetization with (a) concentration of filled iron ions and (b) final content of iron ions.

10(a). In this figure, it is evident that the saturation magnetization is increased with greater primary iron ion concentration. This phenomenon is expected because the amount of the ferrimagnetic magnetite increases with greater primary iron ion concentration in the spinning solution. Moreover, one can recognize that the results show a similar straight line for Sort 1 and a gentle curve for Sort 2. When we compared the results of Sorts 1 and 2, higher magnetization were obtained from Sort 2 than from Sort 1, which agrees with the results of higher yields of magnetite obtained in Sort 2 than in Sort 1.

To quantitatively express the phenomenon just described, the results in Figure 10(a) were replotted against the amount of magnetite (weight percentage of iron ions in fibers) and these results are shown in Figure 10(b). It is evident that the saturation magnetization of these six kinds of fibers increases with the increase in weight percentage of iron ions (contents of magnetite) in the fibers. Because the saturation magnetization of magnetite at room temperature is known to be 92 emu/g,²⁸ the theoretical value of the saturation magnetization of each fiber can be calculated. The experimental values of saturation magnetization are, however, smaller than the theoretical values. Two explanations for this difference are possible: saturation magnetization decreased due to the presence of the paramagnetic phase [hematite and wustite (Fe_{1-x}O)] and saturation magnetization of fine particles generally decreases with small particle size.²⁹ Further investigations on the final formation of iron ions and the

relation between the size and the magnetization of magnetite seem to be necessary for a better understanding of this phenomenon.

CONCLUSION

The *in situ* synthesis of organic particles within polymer matrices is an excellent method to control the mean particle size and size dispersion of a nanoparticle population. With the addition of an NaOH solution, magnetite nanoparticles with an average of 20 nm in diameter can be precipitated *in situ* from both Fe^{2+} and a mixture of $\text{Fe}^{2+}/\text{Fe}^{3+}$ within PVA solutions. The results of experiments show that magnetite nanoparticles were more easily precipitated from a mixture of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions than from Fe^{2+} ions alone. Suitable spinning solutions were obtained with an initial concentration of PVA <4.0 M and a limited final pH value of ~ 8.0 . Magnetic PVA fiber can be successfully obtained by a wet-spinning method with a continuous process because of the homogeneous nanosized particles. Finally, we obtained six kinds of magnetic fibers containing a maximum content of iron ions of 17.63 wt % and the highest magnetization of 13.38 emu/g in fiber 6. This method is versatile and easy to perform, suggesting a wide application to the preparation of nanosized materials with an even distribution. Furthermore, with the combination of the functions of organic nanoparticles and the high forming abilities of polymers, various functional materials could be prepared easily with various forms.

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