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Hybridization and Characteristics of Fe and Fe–Co Nanoparticles with Polymer Particles

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ABSTRACT

Fe and $Fe_{60}Co_{40}$ nanoparticles with mean particle size of about 40 nm were synthesized by hydrogen plasma-metal reaction and then were hybridized in argon atmosphere with nylon and polyethylene particles having mean particle size of 10 and 5 μm, respectively. Particle features and corresponding magnetic properties of the hybrid samples were investigated. After hybridization, Fe and $Fe_{60}Co_{40}$ nanoparticles were successfully coated on the surface of the core particles of nylon and polyethylene, and microstructures of the coated layer are dependent on the mixing ratio of the nanoparticles. The Fe and $Fe_{60}Co_{40}$ nanoparticles after hybridization have no oxidation, structural change, or particle growth, and they maintain their superior magnetic properties.

1. Introduction. Nanoparticles have been extensively studied during this decade. Attention of most studies is focused on synthesis and characteristics, so that a lot of synthesis methods are established and many superior properties are confirmed, which is great encouragement for nanomaterial study.[1−4] However, because nanoparticle materials are usually quite expensive and also difficult to deal with, it has been a subject of much concern how to use them.[5,6] Combining nanoparticle materials with other materials is expected to be a desirable method by which to solve these problems.

There is presently considerable interest in composite technology of nanomaterials. Although several methods were developed to fabricate nanocomposite materials,[7,8] it remains a quite difficult work to get composite spheres consisting of metallic magnetic nanospheres and a polymer core. Usually, nanoparticles aggregate so strongly that it is difficult to disperse them from each other; this is especially true for magnetic nanoparticles. In addition, there are other problems associated with metallic nanocomposites, such as oxidation and growth in particle size. Generally, metallic nanoparticles and clusters are unstable in solution; additionally, polymer particles are unstable at high temperature. Therefore, chemical methods such as liquid reaction and CVD are not available. So far, a complete composite of two or more kinds of nanoparticles is difficult to achieve unless they are mixed during preparation process.[9,10] Film technology is considerable for this kind of work, but the equipment is usually quite complicated and expensive, and the amount of sample treated each time is extremely small. As a result, these methods can be used only in very limited cases. Therefore, exploration of the new methods for coating a metallic layer on a polymer core is valuable.

Koishi developed a hybridization method by which it is possible to achieve the complete composite and also to embed fine particles on the surface of large core particles.[11−13] By using this method, we also successfully coated fine magnetic Fe_3O_4 particles on the surface of polymer core particles.[14] However, hybridization has not been used for composites in nanoscale so far. The next question we are interested in is whether this method is effective for magnetic nanoparticle composition. From previous study,[15,16] it is known that Fe and $Fe_{60}Co_{40}$ nanoparticles, which have bcc structure, exhibit superior hard magnetic properties. They can be conveniently used in magnetic recording if they are successfully coated on the surface of the polymer particle. The purpose of this study is to investigate the composite effect of hybridization on nanoparticles and to study features, structure, and magnetic properties of the hybrid particles.

2. Experimental. Fe and $Fe_{60}Co_{40}$ nanoparticles were prepared by hydrogen plasma-metal reaction (HPMR) and were taken out from the chamber after sufficient passivation.

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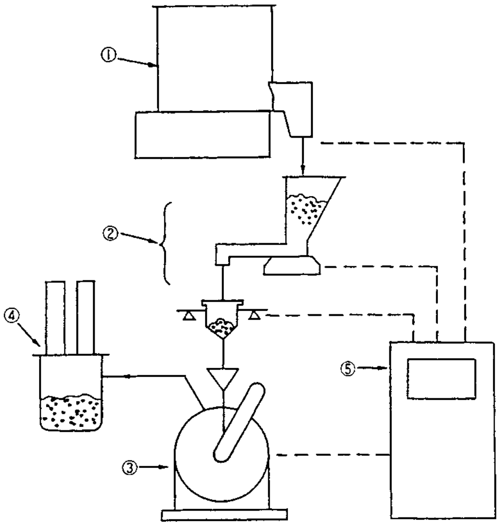

Figure 1. Schematic diagram of the machine used for hybridization, ①the O. M. dizer, ②feeder, ③hybridizer, ④collector and ⑤controller.

The core particles used in this work were spherical nylon $-[NH-(CH)_{11}-CO]_n-$ (mp 380 K, Tore Co., Ltd, SP-500) and spherical polyethylene $-[CH_2-CH_2]_n-$ (T_g 366 K, mp 440 K, Sumitomo Co., Ltd, 2080), which are hereafter expressed as nylon and PE, respectively. The former is in crystalline state and the latter is in amorphous state. A schematic illustration of experiments is described in Figure 1. The polymer particles and metallic nanoparticles are first mixed by a mixing machine called an O. M. dizer, and then the mixture was treated by a machine called a hybridizer, in which nanoparticles are coated onto the polymer particle surface and form composite particles as shown in Figure 2. In this article, we describe this coating and composite process of this hybridization.

The mixing ratios of polymer particles to nanoparticles (by weight) were 100:5 and 100:10. Hybridization was carried out in an argon atmosphere in order to prevent the nanoparticles from oxidation, and the detailed conditions are given in Table 1. The total amount of sample was fixed at 20 g, and hybridization was continued for 5 min at a rotation speed of 13 000 rpm (i.e., 80 m/s in linear speed). The hybrid samples were characterized by X-ray diffraction (XRD) using monochromated Cu Kα radiation. The size distribution and appearance of particles were observed by transmission electron microscopy (TEM) using a 200 kV Hitachi H-800 microscopy and scanning electron microscopy (SEM). To investigate the distribution of the coating particles on the surface of a core particle, distribution of Fe and Co elements was observed by electron probe microanalysis (EMPA). The sample for EMPA observation was prepared by mixing the hybrid particles into an epoxide resin adhesive and mechanically polishing it with emery papers after hardening. The magnetic properties were measured by vibrating sample magnetometer (VSM) with applied field up to 15 kOe.

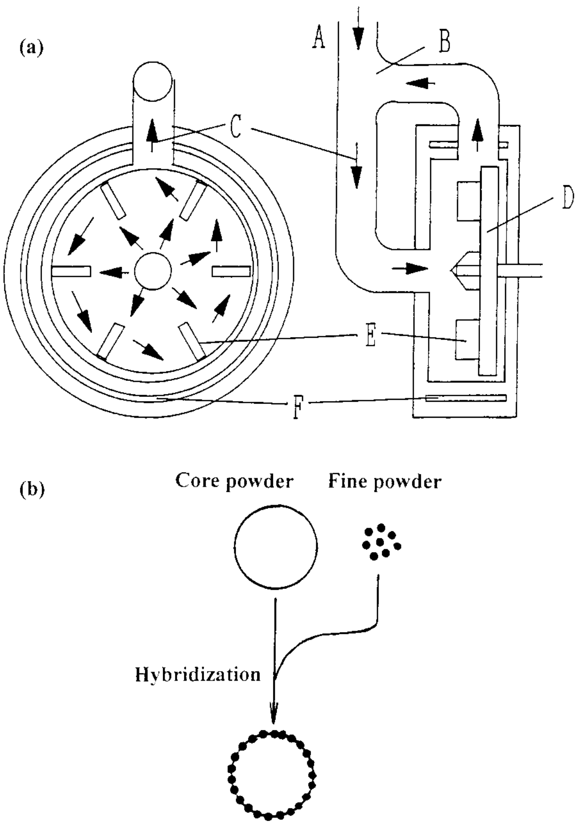

Figure 2. Schematic diagram of hybridizer (a) (A: feed chute, B: circulation route, C: trace of powder, D: rotor, E: striking pin, F: jacket) and (b) model of hybridization process.

Table 1: Condition of Hybridization, Recovery Ratios, and Magnetic Properties of the Hybrid Particles

coating particles	coating particles	mixing ratio (wt.)	rotation speed (rpm)	recovery ratio (%)	M_s (emu/g)	H_c (Oe)
Fe	nylon	100:5	13000[a]	61.0	188.9	341.9
Fe	nylon	100:10	13000	77.5	172.5	338.3
Fe	PE	100:5	13000	58.0	180.1	337.6
Fe	PE	100:10	13000	81.5	177.5	352.9
$Fe_{60}Co_{40}$	nylon	100:10	13000	80.0	189.6	910.1
$Fe_{60}Co_{40}$	PE	100:10	13000	56.5	178.6	1018.8
Fe					157.1	343.2
$Fe_{60}Co_{40}$					194.3	926.6

[a] The corresponding linear speed is 80 m/s.

3. Results and Discussion. As can be seen from Table 1, the recovery ratio, expressed by the weight ratio of the samples before and after hybridization, is higher than 56% and reaches 80% at maximum. The loss is due to remnants in the chamber as well as the collection pipes of hybridizer. The recovery ratio is dependent on the particle's fluid state, gas pressure, and flow rate. It is possible to raise the recovery ratio by adjusting collection conditions and further collecting the remnant.

Figure 3 shows TEM micrographs of Fe (a) and $Fe_{60}Co_{40}$ (b) nanoparticles and SEM micrographs of nylon (c) and PE (d). The Fe and $Fe_{60}Co_{40}$ nanoparticles have nearly spherical shape with mean particle sizes of 45 and 40 nm, respectively. The particles form a chain structure of about 500 nm in length caused by magnetostatic force. As for recording medium, this kind of structure is desirable since the coercive force can be enhanced owing to its shape anisotropy. On the other hand, the chain structure means it is difficult to disperse the particles from each other. Unlike the nanoparticles, the core particles of nylon and PE are spherical with

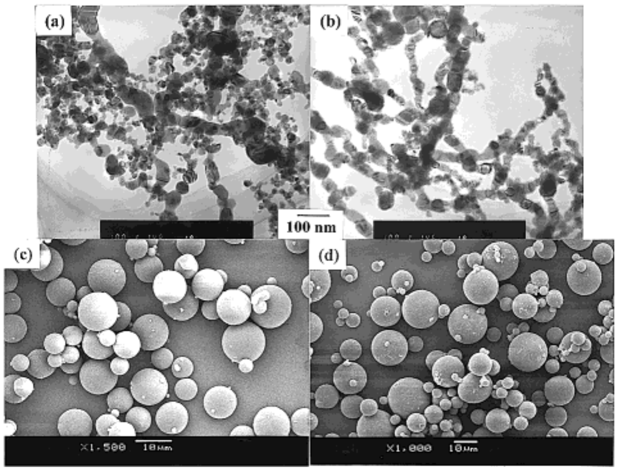

Figure 3. TEM micrographs of Fe (a) and $Fe_{60}Co_{40}$ (b) nanoparticles and SEM micrographs of nylon (c) and PE (d).

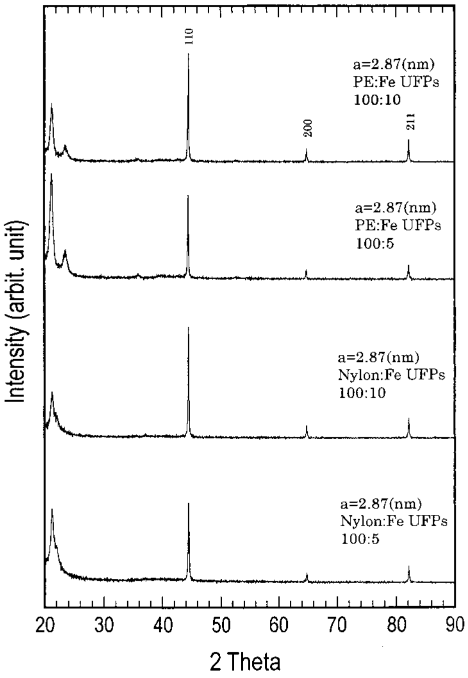

Figure 4. XRD patterns of Fe nanoparticles−hybrid nylon and PE samples in the mixing ratios of 100:5 and 100:10.

a smooth surface and have mean particle diameters of 10 and 5 μm, respectively.

Figures 4 and 5 show XRD patterns of nanoparticle-hybrid polymer particles. All samples are composed of an Fe based phase and a polymer phase, and peaks of an oxide phase are not observed. From our previous studies,[17,18] it is known that metallic nanoparticles are so active that oxidation and ignition phenomena occur easily during heating or mechanical processes. As hybridization is a high-energy treatment, oxidation and ignition are possible to occur. Nevertheless, the nanoparticles after hybridization keep the original bcc structure and have almost the same lattice constants without oxidation. On the basis of these results, we can say that the nanoparticles are stable during hybridization, and we believe this is due to the low oxygen partial pressure in the chamber.

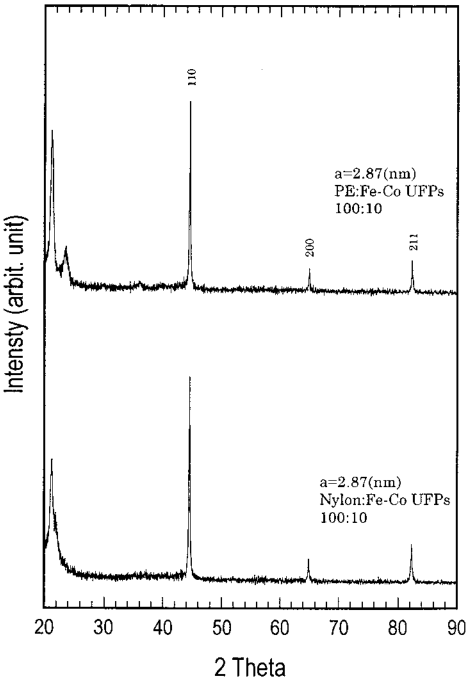

Figure 5. XRD patterns of $Fe_{60}Co_{40}$ nanoparticles−hybrid nylon and PE samples in the mixing ratios of 100:10.

Figure 6 shows SEM micrographs of Fe−nylon composite particles after treatment with the O. M. dizer (a) and hybridizer (b,c) in the mixing ratios of 100:5 and 100:10. As can be seen from Figure 4a, Fe nanoparticles are not coated onto the surface of nylon particles, although they are mixed into nylon particles. This illustrates that the simple mechanical mixing is not enough to break aggregation among Fe nanoparticles. In contrast, Fe nanoparticles after hybridization are successfully coated onto the polymer core surface. Fe nanoparticles on the core surface increase with increasing the mixing ratio of Fe nanoparticles, so it is possible to adjust the microstructure of the coated layer by changing the mixing ratio. It is interesting that Fe nanoparticles are finely dispersed from each other and distribute homogeneously on the core surface. It is also worth noting that Fe nanoparticles have little change in particle size. It is known that metallic nanoparticles have a strong tendency to grow under mechanical or heating treatment. It seems that hybridization is quite different from the conventional ball milling and mixer. By comparison of the results before and after hybridization, it can be concluded that hybridization has a strong effect to disperse the aggregated nanoparticles without changing their crystalline structure and particle size. The same results are also obtained in the case of PE as shown in Figure 7. The feature of the coated layer does not change with the core materials.

Figure 8 shows SEM micrographs of $Fe_{60}Co_{40}$-composite nylon (a, b) and PE (c, d) particles after treatment with the O. M. dizer and hybridizer in a mixing ratio of 100:10. As in the case of Fe nanoparticles, the nanoparticles before hybridization aggregate without coating on the polymer core surface. The nanoparticles after hybridization are homogeneously coated on the core surface without growth in particle size.

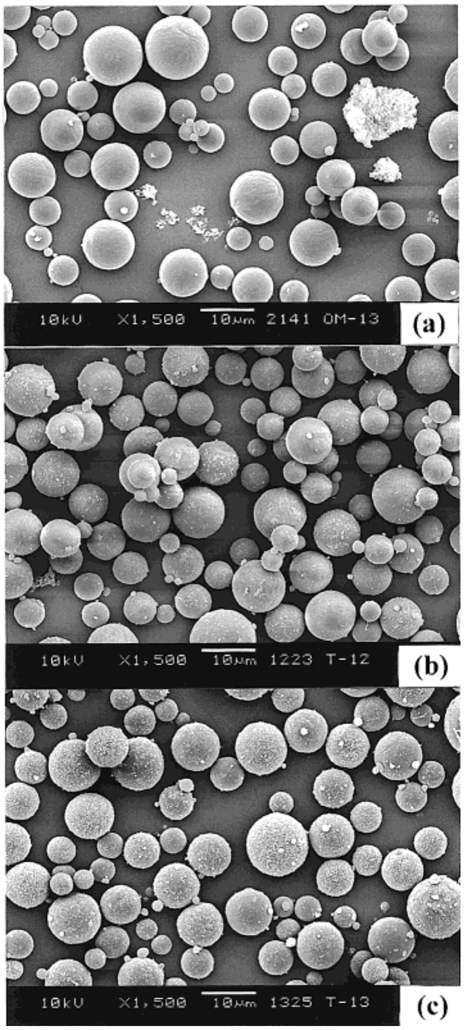

Figure 6. SEM micrographs of Fe nanoparticle composites with nylon particles after the O. M. dizer (a) and after hybridization in the mixing ratios of 100:5 (b) and 100:10 (c).

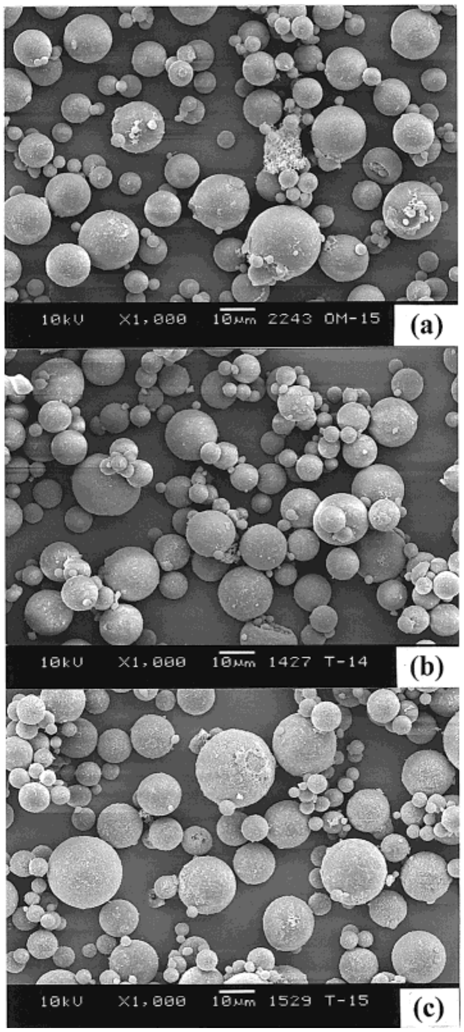

Figure 7. SEM micrographs of Fe nanoparticle composites with PE particles after the O. M. dizer (a) and after hybridization in the mixing ratios of 100:5 (b) and 100:10 (c).

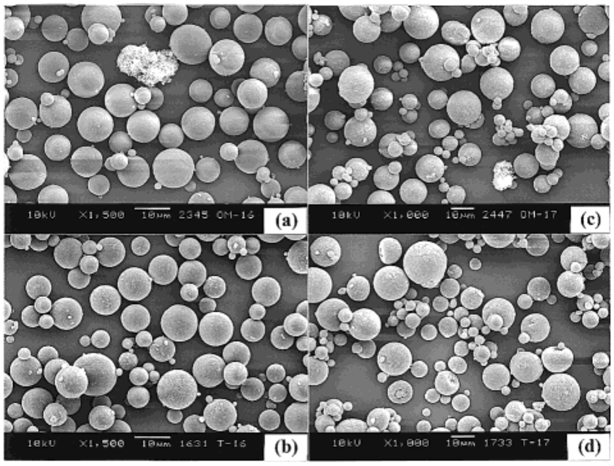

Figure 8. SEM micrographs of $Fe_{60}Co_{40}$ nanoparticle composites with nylon particles after the O. M. dizer (a) and hybridization (b) and with PE particles after the O. M. dizer (c) and hybridization (d).

In comparison to Fe_3O_4 fine particles,[14] aggregation of the nanoparticles is more serious. The aggregation is dependent on attractive forces between particles. As both the Fe and $Fe_{60}Co_{40}$ nanoparticles are much finer in particle size and stronger in magnetism than Fe_3O_4 fine particles, the van der Waals, electrostatic, and magnetostatic forces among nanoparticles are stronger, which leads to a difficulty in dispersion. Treatment of the O. M. dizer is a milling process in which particles move along with a stirrer. This process has a malleability effect, but it has only a weak dispersion effect on particles as particles mainly accept continuous shear stress instead of collision. In hybridization, however, the aggregated particles move quickly and moreover freely in the chamber, and they can be dispersed from each other when a collision takes place.

To see distribution of the nanoparticles on a core particle, the cross sectional micrographs and the characteristic X-ray images of Fe and Co were observed, which are given in Figure 9. In both cases of Fe and $Fe_{60}Co_{40}$ nanoparticles, the Fe or Co element homogeneously distributes around the core section, indicating that the nanoparticles homogeneously distribute on the core surface. In combination with Figures 6−8, it can be concluded that hybridization is very fit to nanocomposites of inorganic and organic materials. So far good hybridization results were achieved only when the

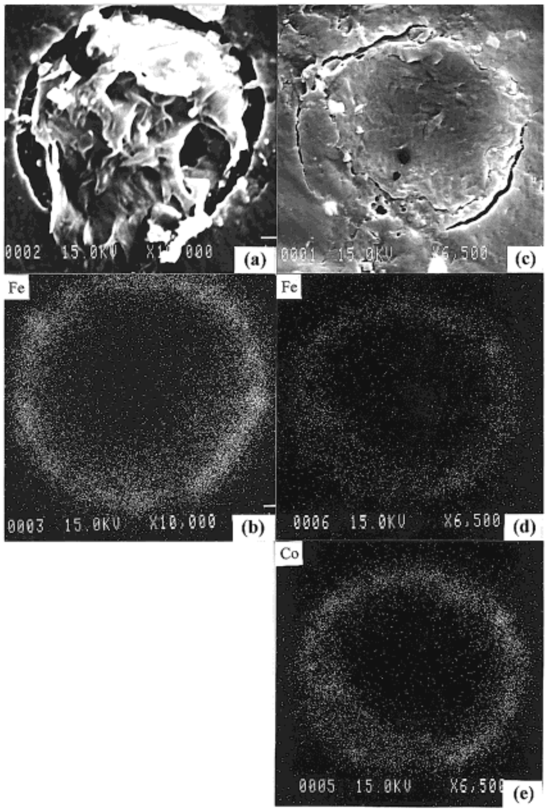

Figure 9. Cross sectional micrographs and the characteristic X-ray images of Fe and Co; (a) and (b): Fe nanoparticle−hybrid nylon particle; (c), (d), and (e): $Fe_{60}Co_{40}$ nanoparticles−hybrid nylon particle.

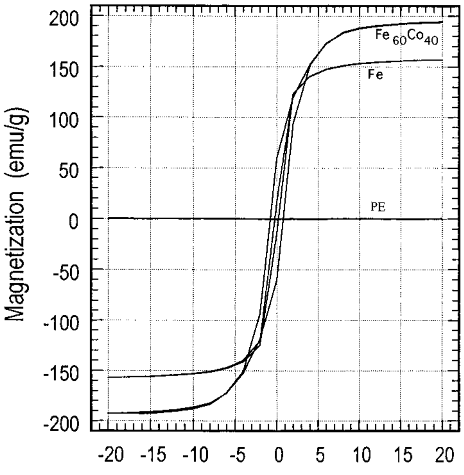

Figure 10. Magnetization curves of PE, Fe, and $Fe_{60}Co_{40}$ nanoparticles.

radius ratio of the core particles to the fine particles is in the range from 5 to 10.[19,20] Our results illustrate that the good hybridization results can also be achieved even when the radius ratio is high, up to 100.

Figure 10 shows magnetization curves of PE, Fe, and $Fe_{60}Co_{40}$ nanoparticles. PE is paramagnetic, but Fe and $Fe_{60}Co_{40}$ nanoparticles are ferromagnetic with large hysteresis loops and have the saturation magnetization of 175 and 190 emu/g, respectively. As the polymer particles are extremely weak in magnetism compared to the nanoparticles, it is reasonable to neglect the core particle's influence on magnetism. For a comparison with the original nanoparticles, magnetization of the hybrid samples is converted into the contribution of the nanoparticles.

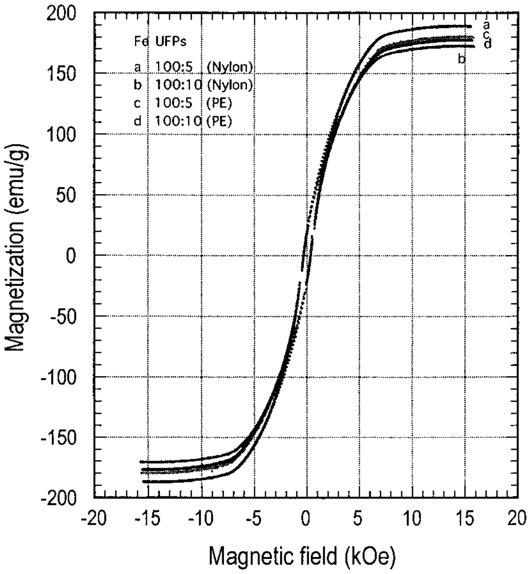

Figure 11. Magnetization curves of Fe nanoparticle−hybrid polymer particles.

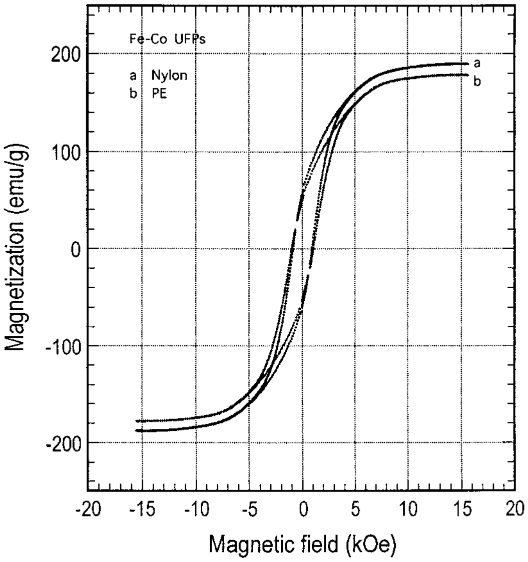

Figure 12. Magnetization curves of $Fe_{60}Co_{40}$ nanoparticle−hybrid polymer particles.

Figure 11 shows magnetization curves of Fe nanoparticle−hybrid polymer particles. The four hybrid samples exhibit ferromagnetism similar to the original Fe nanoparticles. The same results are also obtained in the case of $Fe_{60}Co_{40}$ nanoparticles, as shown in Figure 12. The saturation magnetization (M_s) and the coercive force (H_c) of the samples before and after hybridization are given in Table 1. M_s and H_c are nearly the same as those of the original Fe and $Fe_{60}Co_{40}$ nanoparticles despite a small deviation. The magnetic behaviors demonstrate that the nanoparticles are prevented from oxidation and growth in particle size, being in good agreement with the XRD results in Figures 4 and 5.

Apparently, we are successful not only in preparing nanocomposite materials but also in keeping the original superior magnetic properties of the nanoparticles. Furthermore, it is easy to adjust magnetization of the hybrid samples by changing the mixing ratio, which is usually important in application cases.

4. Conclusions. Fe and $Fe_{60}Co_{40}$ nanoparticles are successfully coated on the surface of polymer core particles by hybridization. Changing the mixing ratio of the nanoparticles can control the microstructure of the coated layer. The hybrid samples keep the original magnetic properties of the nanoparticles without oxidation and growth in particle size.

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