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Materials

Effect of vacuum annealing on the characteristics of composite pellets containing DBSA-doped polyaniline and Fe nanoparticles

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Abstract: The DBSA-PANI-Fe composite powder with 50wt% of Fe nanoparticles was prepared by mechanically mixing the DBSA-doped polyaniline powder and Fe nanoparticles. The composite powder was compacted to pellets and the pellets were annealed in vacuum at 443, 493, 543, and 593 K for 60 and 120 min. The conductivity of the pellet increases markedly with increasing the annealing temperature up to 493 K, and then decreases with further increasing the annealing temperature. When the pellet was annealed at 493 K for 60 min, the increment of conductivity reaches a maximum value, and the conductivity is 2.6 times as large as that of the pellet unannealed. The conductivities of the pellets annealed under the conditions of 543 K/120 min, 593 K/60 min, and 593 K/120 min are lower than the conductivity of the pellet unannealed. For all the pellets, the variation in conductivity with temperature reveals that the charge transport mechanism can be considered to be 1-D variable-range-hopping (1-D VRH). The composite pellet shows a magnetic hysteresis loop independent of the annealing condition. The saturation magnetization is about 5.4×10^4 emu/kg. The saturation field and the coercivity are estimated to be 4.38×10^5 and 3.06×10^4 A/m, respectively. The crystalline structure of Fe nanoparticles in the composites does not change with the annealing condition. The annealing condition cannot destroy the polymer backbones.

Key words: doped polyaniline; dodecylbenzene sulfonic acid (DBSA); Fe nanoparticles; vacuum annealing; structure; conductivity; magnetization

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1. Introduction

Polyaniline (PANI) having both electrical and magnetic behaviors has been intensively investigated because of its potential applications in electrical, magnetic, and electronic devices. PANI composites containing Fe_3O_4 nanoparticles are mostly studied. Wan *et al*. prepared the PANI nanocomposites containing Fe_3O_4 nanoparticles by chemical synthesis methods [1-3]. They found that the nanocomposites had a conductivity from 10 to 10^{-2} S/m, a saturation magnetization from 2×10^3 to 2.0×10^4 emu/kg, and a coercivity of zero. Deng *et al*. [4-5] prepared the Fe_3O_4-PANI nanoparticles with core-shell structure by *in situ* polymerization. The Fe_3O_4-PANI nanoparticles had a conductivity from 1.5×10^{-2} to 9.2×10^{-3} S/m, a saturation magnetization from 4.2×10^3 to 4.8×10^4 emu/kg, and a coercivity from 1.59×10^2 to 4.40×10^3 A/m. Aphesteguy and Jacobo [6] obtained Fe_3O_4-PANI nanocomposites by using a chemical method. The Fe_3O_4-PANI nanocomposites had a higher saturation magnetization of 7.2×10^4 emu/kg and a moderate conductivity of 10^{-2} S/m. Recently, it has been reported that DBSA-PANI-Fe composites were prepared by mechanically mixing DBSA (4-dodecylbenzenesulfonic acid)-doped polyaniline powder and Fe nanoparticles [7]. As the Fe nanoparticle content increased from 30wt% to 70 wt%, the saturation magnetization of the composite increased monotonously from 3.2×10^4 to 7.8×10^4 emu/kg, and the conductivity decreased linearly from 25±2 to 7±1 S/m. According to the results reported previously

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[3-7], as the magnetization behaviors of the composites are improved, their conductivities are degraded. It seems to be difficult to simultaneously obtain high conductivity and high saturation magnetization for the PANI composites containing Fe or Fe_3O_4 nanoparticles. In the present study, the DBSA-PANI-Fe composites were annealed in vacuum to try to obtain the composites with high conductivity and high saturation magnetization. Electrical and magnetic properties of the composite pellets annealed were studied by measuring the conductivity at 190-300 K and the magnetization curve at room temperature as a function of annealing condition. X-ray diffraction (XRD) was used to examine the structure of Fe nanoparticles in the composite pellets. Fourier transform infrared spectroscope (FT-IR) was used to study the molecular structure of the DBSA-PANI-Fe composites.

2. Experimental procedure

The DBSA-PANI powder was prepared by using an emulsion polymerization process [8]. The Fe nanoparticles were prepared by a reverse emulsion polymerization process [9]. The XRD measurement has indicated that the Fe nanoparticle powder consists of nano-size Fe and Fe_3O_4 [7]. The room-temperature conductivity of the Fe nanoparticle pellet is about 2.2×10^{-5} S/m, which is much smaller compared with that of the bulk Fe (1.2×10^{7} S/m). It is considered that the Fe nanoparticle surface is oxidized forming the oxide shell on the nanoparticle surface [10]. The DBSA-PANI-Fe composite powder containing 50wt% Fe nanoparticles was obtained by mechanically mixing the DBSA-PANI powder with Fe nanoparticles at an almost same milling speed in an agate mortar in ambient for 30 min [7]. The composite powder was compacted to the pellets of about 4×10^{-4} m in thickness and 1.3×10^{-2} m in diameter at the same pressure. The pellets were annealed in a vacuum of 3×10^{-3} Pa at 443, 493, 543, and 593 K for 60 and 120 min, respectively.

XRD (D/Max-RB, Rigaku) was used to analyze the structure of Fe nanoparticles in the composite pellets. XRD measurements were performed in a standard θ-2θ scan using Cu K_α radiation filtered by a crystal monochromator (wavelength λ=0.15417 nm). The X-ray source was operated at a power of 40 kV×0.1 A. The scan speed was 0.1°/s and the scan step was 0.02°. FT-IR (670, Nexus) was used to characterize the molecular structure. After and before annealing, the resistance R of the composite pellet was measured at room temperature using the four-point probe technique. The conductivity σ of the composite pellet can be given by [11]

$$\sigma = \frac{1}{\frac{\pi}{\ln 2}\cdot R\cdot d} \tag{1}$$

where $(\pi/\ln2)\cdot R$ is the sheet resistance and d, which was measured in terms of a micrometer, is the thickness of the pellet. After annealing, the room-temperature conductivity of the pellets was measured at 20-h intervals for 200 h. For one pellet, an average conductivity could be obtained by calculating the average values of ten-time measurements. The variation in conductivity with temperature was measured from 190 to 300 K by using a four-point probe technique (CFM-5T, Cryogenic). Magnetic hysteresis loops of DBSA-PANI-Fe composite pellets with a square size of about 3 mm×3 mm were measured at room temperature using an alternating gradient magnetometer (AGM, Princeton Measurement). The magnetic field was applied along the pellet plane.

3. Results and discussion

Fig. 1 shows the XRD spectra of the DBSA-PANI-Fe composite pellets unannealed and annealed at various temperatures. As can be seen from Fig. 1, the XRD spectra mainly show the diffraction peaks of Fe(110), Fe(200), and Fe(211). The peaks of Fe_3O_4 can be also seen. It is similar to the XRD spectra of Fe nanoparticles [7]. The size D of Fe and Fe_3O_4 particles can be given by the Scherrer's equation as following:

$$D = \frac{0.89\lambda}{\beta\cos\theta} \tag{2}$$

where λ is the X-ray wavelength, β the half-height width of the X-ray diffraction peak, and θ the Bragg angle. Using Eq. (2), according to the β values of the Fe and Fe_3O_4 peaks, the average particle sizes of Fe and Fe_3O_4 were calculated. The particle sizes of Fe and Fe_3O_4 are independent of annealing temperature and are about 24 and 13 nm, respectively. The Fe and Fe_3O_4 particles have a nano-size. This result is consistent with that of the Fe nanoparticle powder [7]. Furthermore, a ratio of the highest Fe peak to the highest Fe_3O_4 peak does not markedly change with annealing temperature. These results mean that annealing does not change the structural behaviors of the Fe nanoparticles in the DBSA-PANI-Fe composite.

Fig. 2 shows the FT-IR spectra of the DBSA-PANI-Fe composite pellets unannealed and annealed at various temperatures. Fig. 2(b) shows a part of the FT-IR spectra shown in Fig. 2(a). As can be seen from Fig. 2(a), the peak positions except for the peak at about 1460 cm^{-1} are independent of the annealing condition. The peak at about 1460 cm^{-1} is characterized by benzene ring stretching and that at about 1556 cm^{-1} is related to the quinone structure [12-14]. It demonstrates that the aromatic structure of polyaniline is retained in all the DBSA-PANI-Fe composites. As can be seen from Fig. 2(b), as the annealing temperature increases, the peak at 1467 cm^{-1} in the pellet unannealed broadens and separates markedly into two peaks at 1457 and 1479 cm^{-1}. After the DBSA-PANI-Fe composite pellets are annealed, the peak at 1479 cm^{-1} can be attributed to the fact that some of the acids in the DBSA-doped polyaniline area have been transformed to the de-doped form and the dopants have segregated from the polymer backbones [12, 15]. On the other hand, it has been suggested that the interaction between PANI and Fe_3O_4 nanoparticles exists in the PANI-Fe_3O_4 composites [4, 16-18]. The interactive mechanism may be the interaction of the 3d orbit of a Fe atom with lonepair electrons of a N atom in the PANI chain to form a coordinate bond [4, 18]. Therefore, it is considered that the peak at 1457 cm^{-1} may be attributed to the interaction between DBSA-PANI and Fe or Fe_3O_4 nanoparticles.

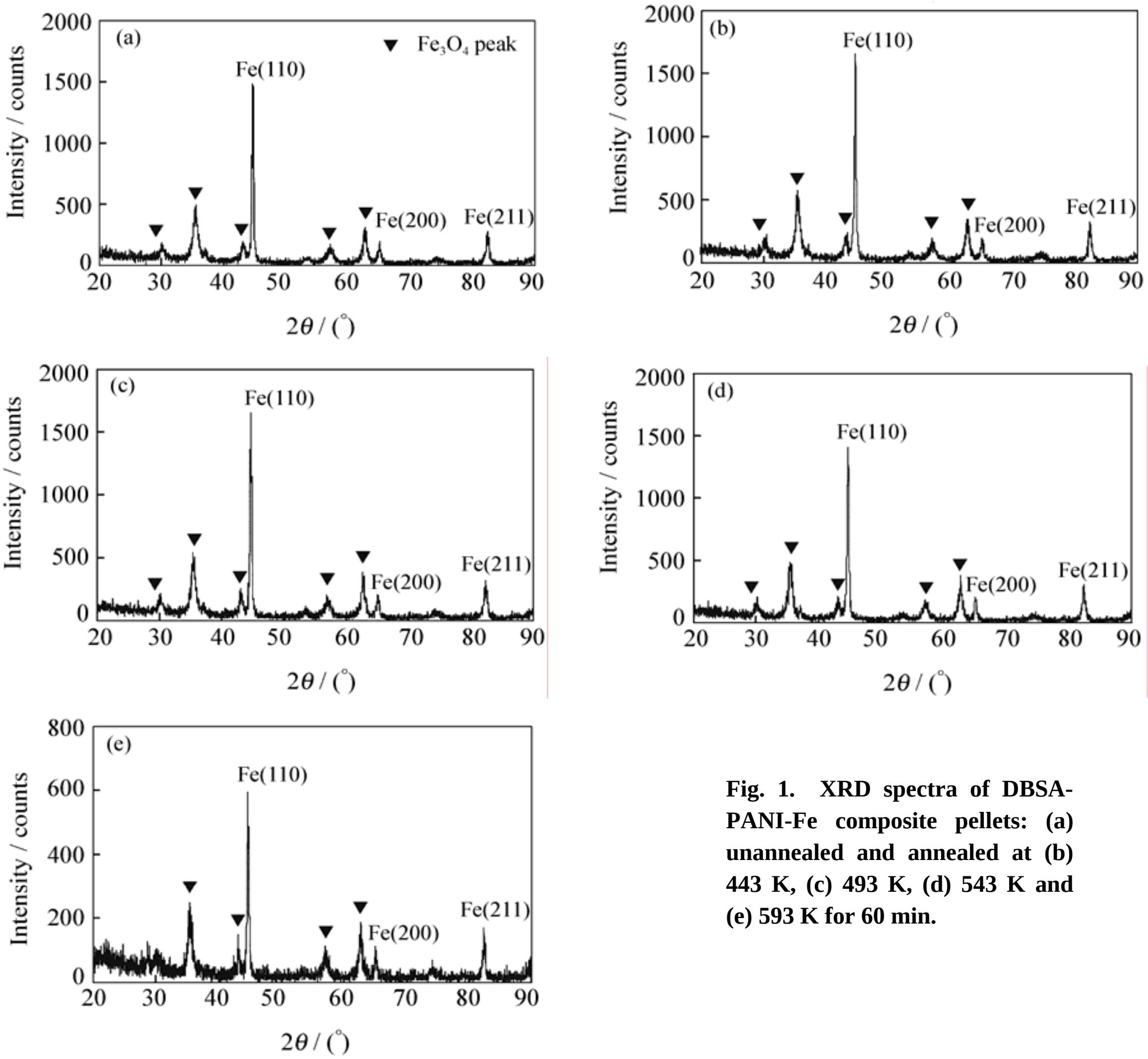

Fig. 1. XRD spectra of DBSA-PANI-Fe composite pellets: (a) unannealed and annealed at (b) 443 K, (c) 493 K, (d) 543 K and (e) 593 K for 60 min.

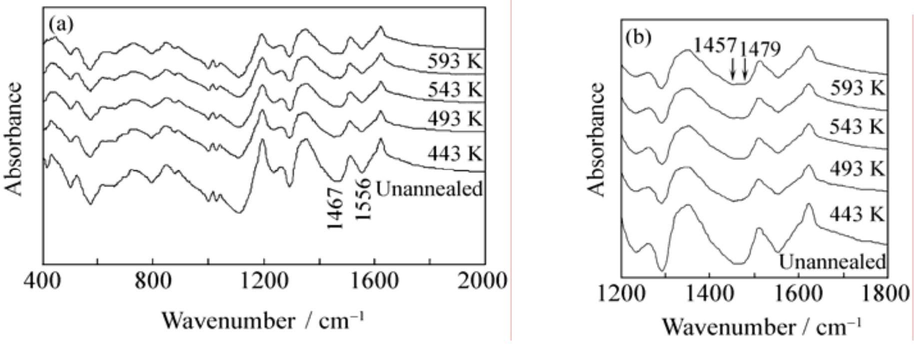

Fig. 2. FT-IR spectra of DBSA-PANI-Fe composite pellets unannealed and annealed at various temperatures (a) and a part of the FT-IR spectra of Fig. 2(a) (b).

Fig. 3 shows typical relationships between the voltage and current in DBSA-PANI-Fe composite pellets unannealed and annealed at 593 K for 120 min. As seen from Fig. 3, the voltage increases linearly with increasing the current, indicating that the DBSA-PANI-Fe composite pellets represent an ohmic characteristic. All the composite pellets annealed exhibit the ohmic characteristic. The slope of the straight line in Fig. 3 gives the resistance R of the specimen. The conductivity σ was calculated in terms of Eq. (1). According to Eq. (1), it can be said that the ratio of the conductivity σ_A of the pellet annealed to the conductivity σ_B of the pellet unannealed is equal to the ratio of the resistance of the pellet unannealed to that of the pellet annealed. Fig. 4 shows the variation in the conductivity ratio σ_A/σ_B with annealing temperature for the annealing time of 60 and 120 min. As seen from Fig. 4, the conductivity ratio increases initially with increasing the annealing temperature up to 493 K and then decreases with further increasing the annealing temperature. When the composite pellet is annealed at 493 K for 60 min, the increment of conductivity reaches a maximum value and the conductivity is 2.6 times as large as that of the pellet unannealed. For the annealing time of 60 min, only the annealing of 593 K results in a decrease in conductivity relative to the pellet unannealed. However, for the annealing time of 120 min, the conductivity of the pellets annealed is smaller than that of the pellet unannealed when the annealing temperature reaches and exceeds 543 K.

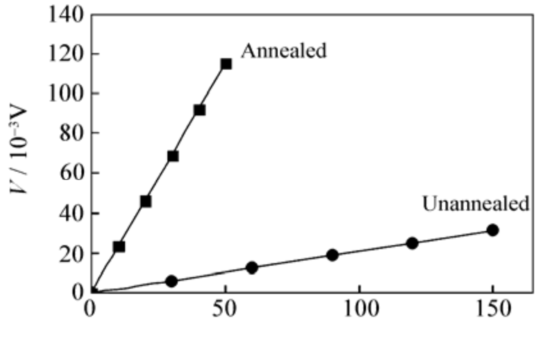

Fig. 3. Typical relationships between voltage and current in DBSA-PANI-Fe composite pellets unannealed and annealed at 593 K for 120 min.

Fig. 5 shows a variation in conductivity with temperature for DBSA-PANI-Fe composite pellets annealed at 493 and 593 K for 60 min. As can be seen from Fig. 5, the conductivity increases with increasing temperature. It means that the pellets represent a temperature dependence of conductivity similar to a semiconductor.

In the variable-range-hopping (VRH) model, the temperature T dependence of conductivity σ follows the following relation:

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{\frac{1}{r}}\right] \tag{3}$$

where T_0 is the Mott characteristic temperature, and σ_0 the conductivity at $T=\infty$. T_0 and σ_0 are determined by the localization length, the density of state, and the hopping distance in the material. The r is determined by the dimension of the researching system. For the 1-D, 2-D, and 2-D systems, r is equal to 2, 3, and 4, respectively. In the 1-D VRH model, Eq. (3) can be expressed as

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{\frac{1}{2}}\right] \tag{4}$$

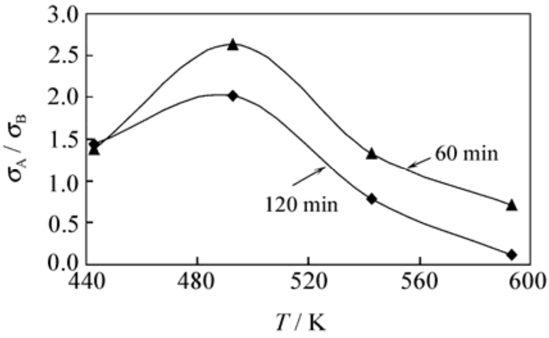

Fig. 4. Variation in the conductivity ratio σ_A/σ_B with annealing temperature for DBSA-PANI-Fe composite pellets annealed for 60 and 120 min.

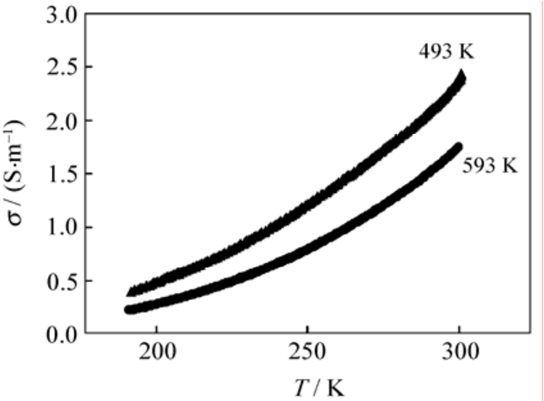

Fig. 5. Variation in conductivity with temperature for DBSA-PANI-Fe composite pellets annealed at 493 and 593 K for 60 min.

Fig. 6 shows the temperature dependence of conductivity of the pellets, plotted as lnσ *versus* $T^{-1/2}$. As can be seen from Fig. 6, the plot exhibits a well linear dependence having a linearity factor larger than 0.9998. It indicates that the 1-D VRH model is suitable for explaining the charge transport mechanism of the composite pellets annealed. It is reported that the charge transport mechanism of the DBSA-PANI-Fe composite pellet and the DBSA-PANI pellet can be explained by the 1-D VRH model [7-8]. The annealing does not change the charge transport mechanism in the DBSA-PANI-Fe composite pellets. The DBSA-PANI is the conductive region in the DBSA-PANI-Fe composite pellet because the conductivity of the DBSA-PANI is very high compared with Fe nanoparticles. As a result, 1-D VRH can also control the charge transport in the DBSA-PANI-Fe composite pellet.

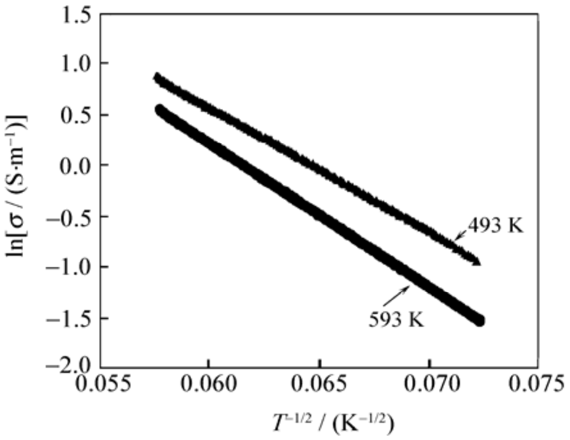

Fig. 6. Temperature dependence of the conductivity of the pellets plotted as lnσ *versus* $T^{-1/2}$.

The vacuum-annealing at a high temperature for a long time resulted in the degradation of the conductivity of DBSA-doped PANI pellets [15]. The vacuum-annealing condition of 413 K/15 min could markedly decrease the conductivity of the DBSA-doped PANI pellets. Furthermore, when the vacuum-annealing temperature reached 593 K and the annealing time exceeded 30 min, the DBSA-doped PANI pellet exhibited an insulating characteristic. However, in the present study the conductivities of DBSA-PANI-Fe composite pellets annealed at 443 and 493 K are larger than the conductivity of the pellet unannealed. Furthermore, the DBSA-PANI-Fe composite pellet annealed at 593 K for 120 min well retains the ohmic characteristic. These results are very different from those reported previously [15]. The conductivity of the DBSA-PANI-Fe composite pellets exhibits a good thermal stability compared with that of the DBSA-doped PANI pellets.

The Fe nanoparticle pellet has a very low conductivity (2.2×10^{-5} S/m) compared with the DBSA-doped PANI (~10 S/m). Therefore, it is considered that the conductive region in the DBSA-PANI-Fe composite pellet is the area of the DBSA-doped PANI. High temperature vacuum-annealing can result in the degradation of the conductivity of the DBSA-doped PANI [15]. Therefore, when the DBSA-PANI-Fe composite pellets are annealed in vacuum at a high temperature, the conductivity of the DBSA-doped PANI area can decrease. In order to understand the increase in conductivity of the composite pellets annealed, the conductivities of the Fe nanoparticle pellets annealed in vacuum at 493 and 593 K for 60 min were measured. The annealing results in a remarkable increase in the conductivity of the Fe nanoparticle pellets. The conductivities of the Fe nanoparticle pellets annealed at 493 and 593 K are 9.6×10^{-2} and 3.2×10^{-2} S/m, respectively. However, the conductivity of the Fe nanoparticle pellets annealed is smaller by two orders of magnitude than that of the BDSA-doped PANI. Therefore, after annealing, the conductivity of the DBSA-PANI-Fe composite pellet is also predominated by the DBSA-doped PANI area. It has been reported that Fe_3O_4 particles are partially reduced during aniline polymerization and they act as a compensating agent for doped PANI chains [16]. It is considered that in this study the Fe_3O_4 near the DBSA-doped PANI area may be partially reduced during annealing and then the PANI chains are doped by Fe ions. As a result, the conductivity of the DBSA-doped PANI area near the Fe_3O_4 and/or Fe increases with annealing. For the DBSA-PANI-Fe composite pellets annealed, the improvement of conductivity and thermal stability may be attributed to the increase in the conductivity of the DBSA-doped PANI area near the Fe_3O_4 and/or Fe. The reason that annealing could increase the conductivity of DBSA-PANI-Fe composite pellets should be further studied in detail.

Fig. 7 shows the magnetization curves of DBSA-PANI-Fe composite pellets unannealed and annealed at 443, 493, 543, and 593 K for 60 min. As can be seen from Fig. 7, all the DBSA-PANI-Fe composite pellets show a magnetic hysteresis loop. The saturation field and the coercivity are estimated to be about 4.38×10^{5} and 3.06×10^{4} A/m, respectively. The magnetic particles in the composite pellets have nano-size

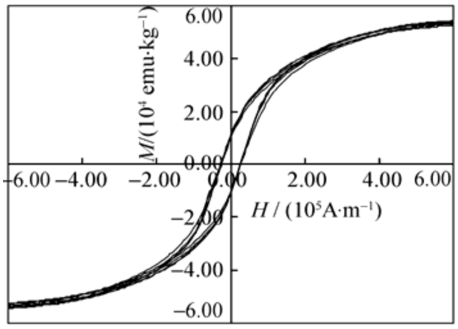

Fig. 7. Magnetic hysteresis loops of the DBSA-PANI-Fe composite pellets unannealed and annealed at 443, 493, 543, and 593 K for 60 min.

and are separated from each other. The exchange interaction between the magnetic nanoparticles is weakened. Therefore, the DBSA-PANI-Fe composite pellets have the high saturation field. The saturation magnetization is about 5.4×10^4 emu/kg. The residual magnetization ratio, *i.e.*, the ratio of the residual magnetization to the saturation magnetization, is about 0.2. The magnetic behaviors are independent of the annealing condition.

4. Conclusions

DBSA-PANI-Fe composite pellets containing 50wt% Fe nanoparticles were annealed in vacuum at 443, 493, 543, and 593 K for 60 and 120 min, respectively. The annealing lower than 543 K could increase the conductivity of the composite pellet. When the pellet was annealed at 493 K for 60 min, the increment of conductivity reached the maximum value and the conductivity was 2.6 times as large as that of the pellet unannealed. The composite pellet showed the magnetic hysteresis loop and the magnetization behaviors were independent of the annealing condition. The saturation magnetization was about 5.4×10^4 emu/kg. The saturation field and the coercivity were 4.38×10^5 and 3.06×10^4 A/m, respectively. The structure of Fe nanoparticles in the composites did not change with the annealing condition. The annealing condition could not destroy the polymer backbones. After annealing, the interaction between the PANI and Fe nanoparticle existed in the DBSA-PANI-Fe composites.

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