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Dielectric behavior and magnetic properties of poly(styrene-co-acrylic acid)metal microspheres

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Abstract

Poly(styrene-co-acrylic acid)metal (P(St-co-AA)metal) particles were prepared by chemical metal deposition. Characterization was carried out by transmission electron microscopy and X-ray diffraction. Dielectric behavior and determination of magnetic properties of P(St-co-AA)metal microspheres were investigated. Thermogravimetric analysis showed that the Curie temperature (T_C) of P(St-co-AA)metal was lower than the T_C of the corresponding block metal and fine metal particles. The susceptibility and hysteresis loop of P(St-co-AA)metal were studied. The results showed that the composite particles are soft magnetic materials.

1. Introduction

Polymer inorganic composite materials have been extensively studied. For example, many attempts have been made to prepare composite particles with polymer as core and inorganic materials as shell [1,2], to generate new materials having the functions of inorganic materials and polymers. These are expected to be used as a toner for xerography or laser printer, dry paints, drug delivery, medical diagnostic tests, and other areas [3].

Composite microspheres coated by fine metal particles can be prepared by mechanical and chemical methods. Mechanical methods, such as a high-speed-stirred mixer or a high-shear mill, have been used for the preparation of microspheres containing metal particles [4]. Chemical methods, for example suspension polymerization [5,6] or emulsion polymerization [7], were used to prepare polymer particles, and subsequently chemical metal deposition [8–10] was carried out for coating metal particles on the surfaces of the polymer microspheres. Thus in this work, dielectric properties, Curie temperature (T_C), hysteresis loop, and magnetic properties of composite particles were studied. We have prepared monodispersed polymer particles using emulsifier-free emulsion polymerization and then formed composite particles using a chemical metal deposition method.

2. Experimental

2.1. Materials

Styrene (St, CR, Central Chemical Plant of Shanghai Chemical Reagent Station) was distilled at 40°C/14.5 mmHg and stored at 4°C. Acrylic acid (AA, chemical reagent, Wulian Chemicals of Shang-Hai) was distilled at 40°C/12 mmHg before use. Ammonium persulfate (APS, Beijing Chemical Plant) was analytical grade and used without further purification. Tin chloride dihydrate ($SnCl_2 \cdot 2H_2O$, Shanghai Fourth Chemical Plant), palladium chloride ($PdCl_2$, Dahao Chemical Plant of Guangdong), nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, Yixin Second Chemical Plant of Jiangsu), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, Shanghai Second Chemical plant), and sodium hypophosphite monohydrate ($NaH_2PO_2 \cdot H_2O$, Taicang Second Chemical Plant of Jiangsu) were analytical grade and used without further purification.

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Table 1
Recipe of the emulsifier-free emulsion polymerization for P(St-co-AA) latex[a]

Ingredient	Seed	Second-stage feed	Total
St (g)	2.4	17.6	20.0
AA (g)	0	4.0	4.0
APS (g)	0.0144	0.0816	0.0960
H_2O (g)	158.5	17.5	176.0

[a] Polymerization conditions: temperature = 70°C; stirrer speed = 350 rpm.

2.2. Preparation of poly(styrene-co-acrylic acid) microspheres

A typical recipe of preparing P(St-co-AA) microspheres is provided in Table 1. The ingredients except the APS solution were placed in a 250 ml five-neck round-bottom flask equipped with stirrer, reflux condenser, thermometer, nitrogen inlet tube, and feeding funnel. The reaction mixture was purged with nitrogen for 1 h, and then the APS solution was added. After the emulsifier-free emulsion polymerization was performed for 3 h at 70°C, the conversion was above 90%. AA, St, and APS were added into the PSt latex solution. After the addition, the reaction lasted for 3 h, and the conversion reached above 90%. The resulting latex solution was cooled down, then filtered through a glass sinter filter. The filtrate was centrifuged, at 15,000 rpm, for 10 min and the precipitates obtained were dispersed again in water using an ultrasonic bath. The centrifugation procedure was repeated three times.Then, the latex was dialyzed for over one week with changes of deionized water each day.

2.3. Preparation of magnetic microspheres

The preparation of poly(St-co-AA)Nickel (P(St-co-AA)Ni) microspheres was as following: poly(St-co-AA) latex (5 g/50 ml) was dispersed in water (150 ml). Into this dispersion, $SnCl_2 \cdot 2H_2O$ was added, and stirred for 1 h at 45°C, The mixture was separated by centrifugation, and then was re-dispersed in water. The centrifugation–dispersion was repeated three times. The solids obtained were dispersed in water (150 ml), and then an aqueous solution of $PdCl_2$ (10 mg) was added. The obtained emulsion was stirred for 1 h at 70°C. The particles were collected by filtration, and then dispersed in water, and an electroless plating solution-1 (EPS-1) was added. The dispersion was stirred at 70°C for 0.5 h and separated using a filter, and re-dispersed in acetone. The particles obtained were dried at room temperature in vacuum. A black powder resulted. Poly(St-co-AA)Cobalt (P(St-co-AA)Co) particles were prepared by the same procedure with EPS-2.

Nickel hypophosphite (EPS-1): $NiCl_2 \cdot H_2O$: 2.36 g; $NaH_2PO_2 \cdot H_2O$: 2.12 g; $C_4H_4O_6KNa \cdot 4H_2O$: 14.2 g; $NH_3 \cdot H_2O$: 5 ml; H_2O 50 ml
Cobalt hypophosphite (EPS-2): $CoCl_2 \cdot 6H_2O$: 3.43 g; $NaH_2PO_2 \cdot H_2O$: 2.76 g; $C_4H_4O_6KNa \cdot 4H_2O$: 15.02 g; $NH_3 \cdot H_2O$: 5 ml; H_2O 50 ml

2.4. Characterization

The size and morphology of polymer and magnetic microspheres were investigated by H-800 transmission electron microscopy (TEM). The latex particle size was calculated based on the sizes of about 100 particles in different regions of TEM photos. Weight-average diameter (D) was calculated according to Eq. (1).

$$D = \sum n_i d_i^3 \Big/ \sum n_i d_i^2, \tag{1}$$

where n_i is the number of particles with diameter d_i. X-ray diffraction of the composite particles was performed on D/max-γA.

2.5. Properties

Magnetic measurements at room temperature were performed with a vibration sample magnetometer (VSM, EG&G, Inc., USA). The variation of magnetic susceptibility with temperature was tested on a Model 5210 lock-in amplifier (EG&G Princeton Applied Research). The Curie temperature of the composite particles was measured with a Perkin–Elmer TGA-7 thermogravimetric analysis (TGA) data were collected by placing the weighed sample (5–10 mg) in a magnetic field with increasing temperature (10°C/min) in a controlled, flowing nitrogen atmosphere. The range of temperature was 50–270°C.

The relative permittivity ε' (dielectric constant) and ε'' loss factor) of a sample varied with frequency and were measured with a ZL5 intelligence LCR (Loss angle, Capacitance, Resistance) surveying instrument having a measurement range of 0.01–100 KHz.

3. Results and conclusions

3.1. Characterization

TEM photos of the P(St-co-AA) particles shown in Fig. 1a demonstrated that particles were near monodispersed and spherical. The weight-average diameter d was about 590 nm.

Fig. 1b and c are TEM photos of P(St-co-AA)Ni and P(St-co-AA)Co microspheres respectively. Comparison with particles shown in Fig. 1a indicates that the surfaces of the particles containing metals was not so smooth, and the size of the metal particles is about 10–

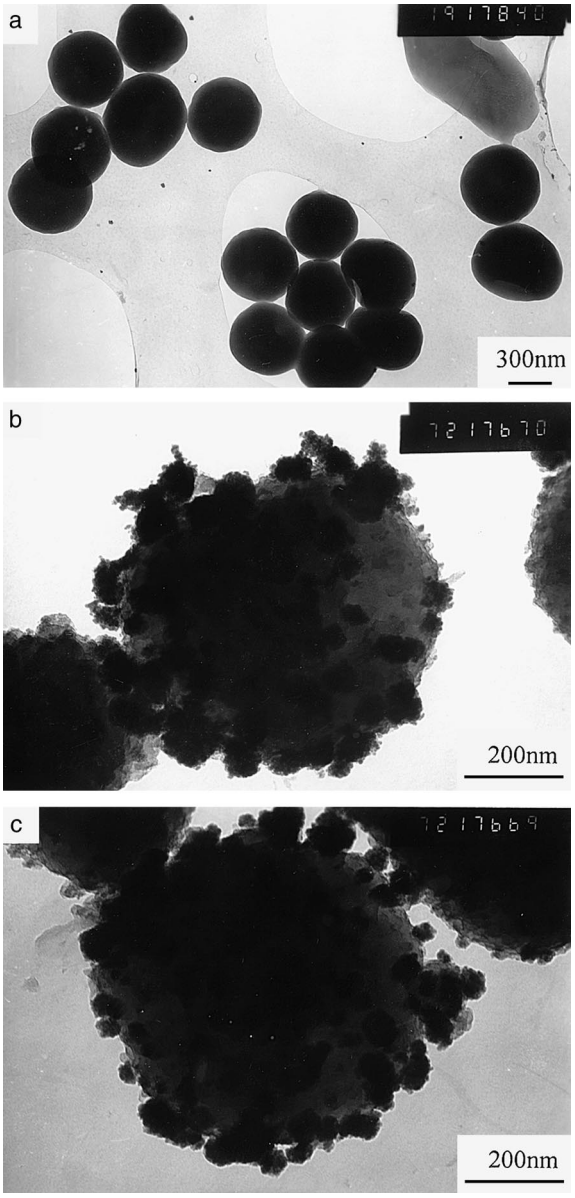

Fig. 1. TEM photos of (a) P(St-co-AA); (b) P(St-co-AA)Ni; (c) P(St-co-AA)Co microspheres.

30 nm. It is very difficult to disperse these magnetic polymer microspheres because of static magnetism between the particles

Fig. 2 shows the X-ray diffraction (XRD) profiles of P(St-co-AA), P(St-co-AA)Ni and P(St-co-AA)Co microspheres respectively. Comparison of Fig. 2a (of P(St-co-AA) microspheres) with Fig. 2b indicates $2\theta = 44.13°$ and 51.67° in Fig. 2b correspond to Ni metal, and $2\theta = 41.34°$, 44.33° and 47.32° in Fig. 2c are attributed to Co metal [11]. Therefore, the small particles on the surfaces of P(St-co-AA)Ni and P(St-co-AA)Co are the

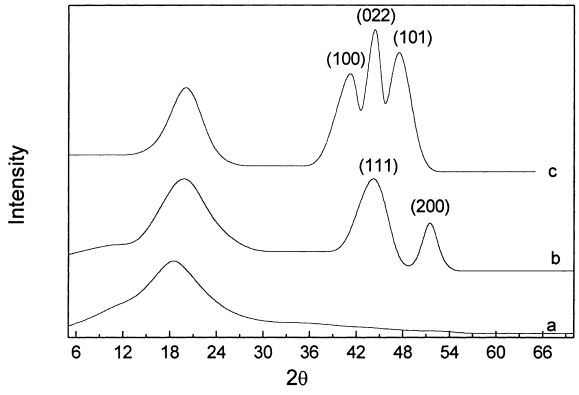

Fig. 2. XRD profiles of (a) P(St-co-AA); (b) P(St-co-AA)Ni; (c) P(St-co-AA)Co microspheres.

particles of Ni metal and Co metal respectively. Tamai et al. [12] reported that the emulsifier-free emulsion copolymerization of styrene and hydrophilic monomers resulted in a water soluble polymer, such as polyacrylamide and poly(2-hydroxyethyl methacrylate) as shell, and PSt as core [13,14]. Therefore, we can imagine that PAA was located on the surface layer of the particles, and the Ni or Co particles formed were attracted by AA on the surface of microspheres. TEM observations confirmed this interpretation.

3.2. Magnetic properties

The alternating magnetic susceptibility of P(St-co-AA)Ni and Co, (χ), as a function of temperature, is shown in Fig. 3. It was observed that as the temperature decreased the alternating magnetic susceptibility also decreased. Thus, P(St-co-AA)Ni and P(St-co-AA)Co magnetic microspheres are not paramagnetic substances. Generally, the paramagnetic substance accords with the Curie–Weiss law:

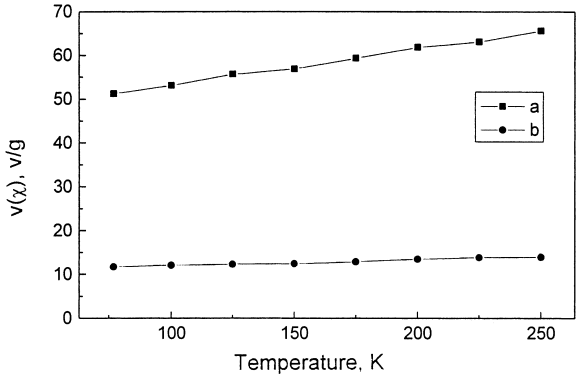

Fig. 3. The alternating susceptibility χ of (a) P(St-co-AA)Ni and (b) P(St-co-AA)Co microspheres vs temperature.

$$\chi = \frac{C}{T - T_C}, \quad (2)$$

where C is the Curie constant, T_C is the Curie temperature.

The value of χ of magnetic microspheres is not only positive but also large. Therefore, the two kinds of magnetic microspheres are ferromagnetic materials. Comparing to the P(St-co-AA)Co magnetic microspheres, the P(St-co-AA)Ni microsphere were easily magnetized because of higher magnetic susceptibility.

According to the value of the coercive force (H_c), a ferromagnetic substance is classified into two types. One is a soft magnetic material, whose coercive force is small and the magnetic hysteresis loop is long and narrow. Another is a hard magnetic material, whose coercive force is large (10^2–10^4). The remnant magnetic induction is large and the magnetic hysteresis loop is wide. It can be inferred from Fig. 4 that the magnetic polymer microspheres can be classified as soft magnetic materials. The soft magnetism of P(St-co-AA)Ni microspheres is superior to P(St-co-AA)Co microspheres (Table 2).

Fig. 5 shows TG curves of P(St-co-AA)Ni, after the particles were heated to 300°C, then cooled to the room temperature, and heated again. Fig. 5a and b represent the first and second heating TG curves of P(St-co-AA)Ni microspheres respectively. The Curie temperature of cobalt (1122.8°C) is very high. The T_C of P(St-co-AA)Co could not be obtained because of decomposition of the polymer at this temperature. In the same experimental condition, the Curie temperature of a block nickel metal was 355°C (in general, 354°C). The

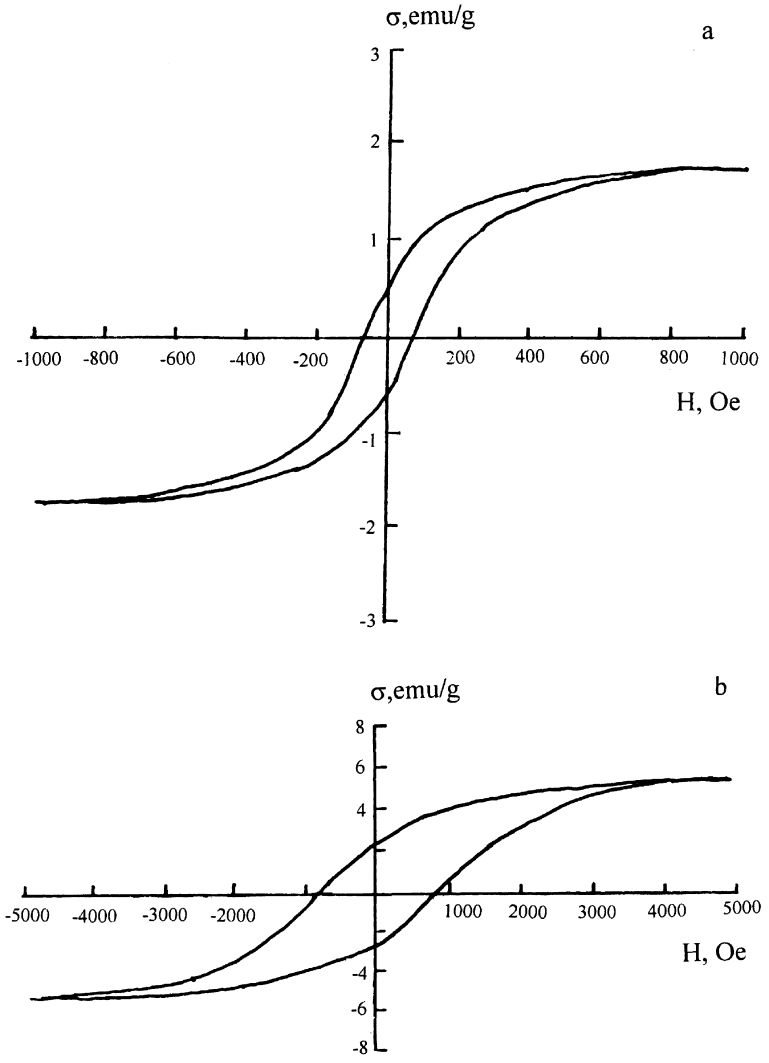

Fig. 4. The magnetic hysteresis loop of (a) P(St-co-AA)Ni microspheres and (b) P(St-co-AA)Co microspheres.

Table 2
Magnetic properties of P(St-co-AA)metal microspheres

	Metal content (wt.%)	χ_i (V/g)[a]	H_c(Oe)[b]	σ_r (emu/g)[c]	σ_s (emu/g)[d]
P(St-co-AA)Ni	10.45	67.00	32.00		1.79
P(St-co-AA)Co	11.76	14.42	700.00	2.4	5.4

[a] Alternating susceptibility in room temperature.
[b] Coercive force.
[c] Remanent magnetization intensity; the remanent magnetization intensity of P(St-co-AA) is too small to measure.
[d] Saturated magnetization intensity.

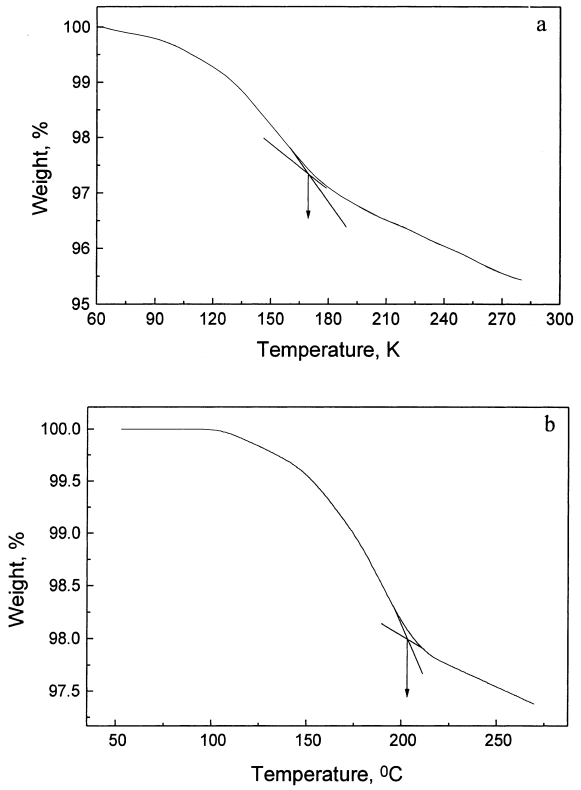

Fig. 5. TGA curves of P(St-co-AA)Ni microspheres in the magnetic field, during (a) the first heating and (b) the second heating.

Curie temperature of P(St-co-AA)Ni microspheres in the first and second heating processes are 175°C and 204°C respectively (see Fig. 5).

Youwei Du, et al. [15] discovered that the Curie temperature (350°C) of fine nickel particles (85 nm) was the same as that of the block nickel. As the size of the nickel particles decreased to 9 nm, the Curie temperature become 300°C. They suggested that this is due to a nanometer effect of the fine particles. In our work, the Curie temperature of magnetic polymer microspheres is not only lower than the block nickel, but also lower than the nanometer nickel particles. Usually, the Curie temperature is proportional to the exchange integral (J). Due to the polymer particles, the composite microsphere had a super exchange between electrons of a magnetic atom compared to the direct exchange in the block nickel metal (the exchange integral is a weakness). On the other hand, the motion of polymer chain segments in the composite microspheres started at the glass transition temperature (T_g), and thermal movement of magnetic particles on the surface of the polymer microspheres became stronger than that of the block nickel and the fine nickel particle. Thus, the spontaneous magnetization of the composite particles disappeared more easily, resulting in a lower Curie temperature. In our previous work, the same phenomenon was found in a P(St-co-4VP)metal system.

Youwei Du, et al. [15] discovered that σ_s–T circle profiles of a sample with 9 and 13 nm during the increasing and decreasing temperatures were not coincidental. The obtained Curie temperature was close to that of the sample with 85 nm. They suggested that this was the result of the growth of particles during increasing temperature, which was verified by their TEM photos as the diameter of particles became larger and their shape became irregular. In our work, the Curie temperature of P(St-co-AA)Ni magnetic microspheres in the second heating was higher than that in the first heating, but both were lower than the Curie temperature of the block nickel and fine nickel particles. The probable reason is that the attraction between carboxylic group and Nickel particles prohibited the fine particles from growing to bigger particles during the heating process. Thus, the Curie temperature was not raised to that of the pure fine nickel particles.

3.3. Dielectric behavior

Figs. 6 and 7 show the relationships of the real part (ε') and the imaginary part (ε'') of the dielectric constant with frequency respectively. Values of ε' and ε'' are normalized. Values of ε' of P(St-co-AA), P(St-co-AA)Ni and P(St-co-AA)Co decreased with increase of frequency (see Fig. 6). Fig. 7a shows that the maximum values of ε'' of P(St-co-AA) appeared in succession with the frequency. This infers that the dielectron loss is due

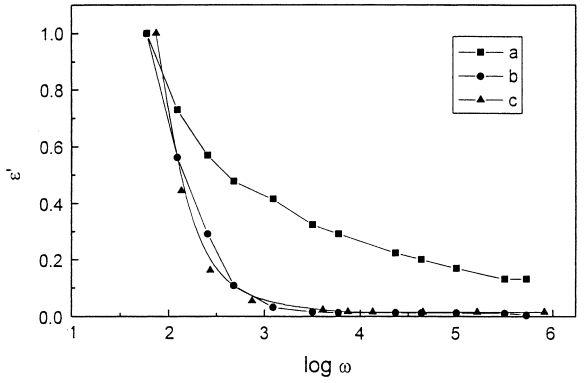

Fig. 6. ε' of (a) P(St-co-AA) particles; (b) P(St-co-AA)Ni particles; (c) P(St-co-AA)Co particles vs frequency.

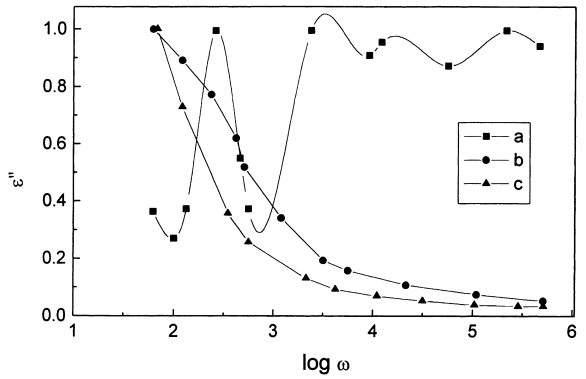

Fig. 7. ε'' of (a) P(St-co-AA) particles; (b) P(St-co-AA)Co particles; (c) P(St-co-AA)Ni particles vs frequency.

to molecular polarization. Various polarization process, such as interface polarization, electron polarization needed different times and could not follow the variation of the electron field. Thus, ε'' appeared as maximum values. If there was no successive polarization, the value of ε'' decreased slowly. Compared with the result of P(St-co-AA), the value of the ε'' of P(St-co-AA)Ni and P(St-co-AA)Co decreased rapidly with increasing frequency. The dielectric loss was caused by electron polarization and conductive polarization (Eq. (3)). The value of ε'' of P(St-co-AA)Ni and P(St-co-AA)Co microspheres is mainly determined by conductive loss due to the existence of metal. Thus, the relationship between the electric loss and frequency can be described by Eq. (3). It is obvious that the ε'' value decreased with increasing frequency.

$$\varepsilon'' = \frac{(\varepsilon_c - \varepsilon_\infty)\omega\tau}{1 + (\omega\tau)^2} + \frac{\sigma}{\omega\varepsilon_0}, \tag{3}$$

where ε_∞ is the dielectric constant when the frequency of the external field goes to infinity, ε_c is the dielectric constant in a static field, τ is the relaxation time of polarization and σ is the conductivity.

4. Conclusions

The results of magnetic susceptibility showed that P(St-co-AA)Ni and P(St-co-AA)Co are ferromagnetic materials; the measurement of the hysteresis loop showed that P(St-co-AA)Ni is easier to be magnetized than P(St-co-AA)Co microspheres. The Curie temperature of composite particles was lower than that of the block nickel metal and the fine nickel particles. The fine nickel particles on a polymer microsphere were not easily aggregated during the heating process, due to the function of carboxylate groups on the surface layer of the particles. The dielectric behavior showed that the dielectric loss of the composite particles was mainly determined by the conductive loss.

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