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The effect of temperature on the electric conductivity of poly(dimethyl siloxane) ferromagnetic gel

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Abstract

In this paper the influence of temperature on the electrical conductivity of a ferromagnetic gel is investigated. The material used was poly(dimethyl siloxane) (PDMS) gel which contained randomly distributed magnetite nanosized particles. The electrical conductivity was measured by means of the two-point dc method. During the heating of the PDMS in the temperature range of 295–460 K the electrical conductivity increased from about 2×10^{-12} to 2×10^{-8} S m⁻¹.

A study of the current–temperature dependence obtained during subsequent heating runs revealed two subranges of temperature characterized by different activation energies. The presence of these subranges could be explained either by the liberation of two different types of charge carrier or by the increase in the degree of polymer cross-linking. In the upper temperature subrange (420–460 K) both types of charge carrier probably contribute to the electrical conductivity of PDMS ferromagnetic gel.

1. Introduction

Ferromagnetic gels belong to a new class of magnetocontrolled elastic materials, which are chemically cross-linked polymer networks swollen with a ferrofluid. The combination of polymers with magnetic materials displays novel and often enhanced properties. It is hoped that ferromagnetic gels will be usable for medical purposes, for example as new electromagnetically induced hyperthermia materials [1]. Other possible applications of ferromagnetic gels include in controlled drug release, construction of artificial muscles and control of enzyme reaction [2–4]. Recently, much attention has been paid to the electrical properties of ferrogels because the presence of metallic particles in organic polymer can enhance its effective electrical conductivity, which depends on the conductivity of particles, and their shape, alignment in the composite, and volume fraction [5, 6]. Particle electric conductivity, in turn, depends on method of preparation, grain size, chemical composition and sintering temperature [7]. In this paper attention is drawn to the temperature effect

on the electrical conductivity of the PDMS ferromagnetic gel. Polymer gels exhibit an abrupt change in volume in response to a small change in such environmental parameters as temperature [8, 9]; therefore their electrical conductivity should be temperature dependent. Additionally, the volume fraction of magnetite in ferromagnetic gel and the average magnetite particle size were determined from magnetization measurements on PDMS ferrogel.

2. Material

As the material, poly(dimethyl siloxane) gel (abbreviated as PDMS gel) was used. The gel contained randomly distributed magnetite (Fe₃O₄) in the form of nanosized particles. The gel was a commercial product with two component reagents, i.e. Elastosil 604 A and Elastosil 604 B, provided by Wacker Co. Component A contained polymeric material and the Pt-containing catalyst, while component B provided the cross-linking agent. Magnetite particles were synthesized by

coprecipitating aqueous solutions of FeCl₂ and FeCl₃ in alkaline solution [10, 11]. The particles were stabilized against agglomeration by adding 1% (w/w) of palmitic acid as a surfactant. After mixing them with the Elastosil 604 B, the cross-linking reaction was carried out at ambient temperature for 24 h to obtain gels. Samples of cylindrical shape and diameter of 10 mm and thickness of about 3.5 mm were prepared just before the experiment and placed in the measuring device.

3. Method

Measurements of electrical conductivity were carried out in the temperature range of 295–460 K during continuous linear heating of samples. Next, samples were cooled without restraint to room temperature and heated again from 295 to 460 K. This procedure was repeated six times, until no further changes in the current–temperature dependence were observed. To check the resistance of the PDMS to heat stress, heating runs were repeated several times. The dc voltage was applied to the samples and the value of the generated electrical field was equal to $2.8 \times 10^3 \text{ V m}^{-1}$. The intensity of the current flowing through the sample was measured during linear changes of temperature.

The sample was locked in the measuring chamber equipped with a heating coil. The heating rate of 1 K min^{-1} was obtained by means of a programmable temperature controller and the temperature was measured using a constantan–copper thermocouple placed close to the sample.

The magnetic hysteresis loop of the ferrogel studied was measured at room temperature with a vibrating sample magnetometer (VSM) made in our laboratory. The device was similar to that built by Foner [12], the inventor of the VSM, and its detailed description can be found elsewhere [13, 14]. The maximum magnetic field, perpendicular to the cylinder axis, was about 1 T.

4. Results and discussion

The hysteresis loop measured for the ferromagnetic PDMS gel by means of the VSM is shown in figure 1. Analysis of the hysteresis loop data yielded values of 2658 A m^{-1} , 3333 A m^{-1} and 199 A m^{-1} for the saturation magnetization, M_s , coercive force, H_c , and remanence magnetization, M_r , respectively.

From the saturation magnetization the volume fraction of the magnetite phase can be determined from the expression

$$\phi_V = \frac{M_s}{M_{\text{grain}}}, \quad (1)$$

where $M_{\text{grain}} = 446 \times 10^3 \text{ A m}^{-1}$ is the spontaneous magnetization of magnetite grains. In the case of PDMS ferrogel, equation (1) leads to a value of 0.6%.

The coercive force, $H_c = 3333 \text{ A m}^{-1}$, proves that the fraction of the magnetic grains reveals, aside from superparamagnetic properties, partly ferromagnetic properties.

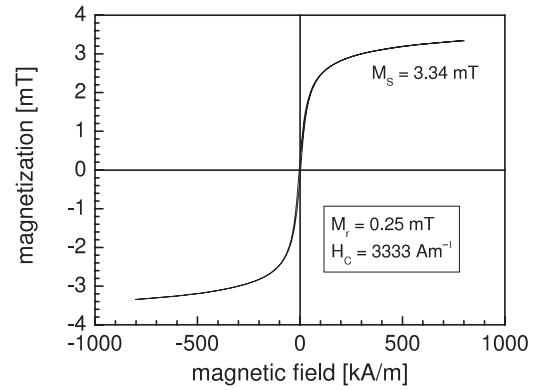


Figure 1. Hysteresis loop of PDMS ferrogel. The values of the saturation magnetization, M_s , coercive force, H_c , and remanence magnetization, M_r , are also shown.

The energy loss during a single cycle, determined on the basis of the surface area of the hysteresis loop, was $W_h = 2.31 \times 10^{-3} \text{ J m}^{-3}$.

The equilibrium magnetization can be expressed as a superposition of the Langevin functions [15]

$$M_L = n \int_0^\infty m(x) L(\xi) f(x) dx, \quad (2)$$

where m and n are the effective magnetic moment and particle number density, respectively, $L(\xi) = \coth(\xi) - 1/\xi$ is the Langevin function with $\xi = \mu_0 m H / k_B T$, μ_0 is the magnetic permeability of vacuum, H is the magnetic field strength, k_B is the Boltzmann constant and T is the absolute temperature.

For the description of the dispersion of magnetite particles the log-normal distribution is usually used [15]:

$$f(x) = \frac{1}{x\beta\sqrt{2\pi}} \exp\left(-\frac{\ln^2(x/x_0)}{2\beta^2}\right), \quad (3)$$

where x is the magnetic diameter, and x_0 and β are the parameters of the distribution function which can be extracted from the magnetization curve. On the basis of these parameters the mean magnetic diameter and standard deviation of particle sizes can be determined. In the case of the log-normal distribution function the moment of p th order can be calculated from the formula

$$\langle x^p \rangle = x_0^p \exp\left(\frac{p^2 \beta^2}{2}\right). \quad (4)$$

The expression for the standard deviation from the mean magnetic diameter $\langle x \rangle$ has the following form:

$$\sigma = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = x_0 \exp\left(\frac{\beta^2}{2}\right) [\exp \beta^2 - 1]^{1/2}. \quad (5)$$

The particle size function of the ferromagnetic gel extracted from VSM measurements is shown in figure 2. The parameters of the above functions are as follows: $x_0 = 8.75 \text{ nm}$, and $\beta = 0.166$. From these values a mean particle diameter of $\langle x \rangle = 8.87 \text{ nm}$, and a standard deviation of $\sigma = 1.5 \text{ nm}$ were determined. On the basis of the

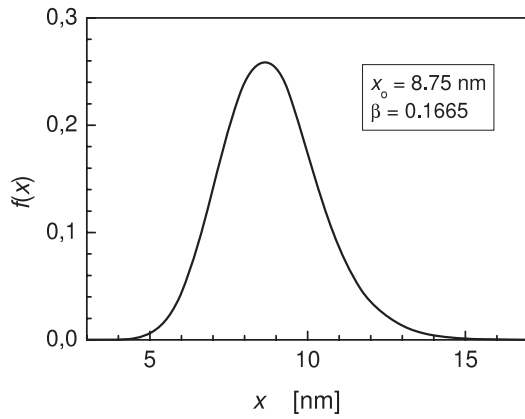


Figure 2. Particle size distribution function in PDMS ferrogel obtained from VSM data.

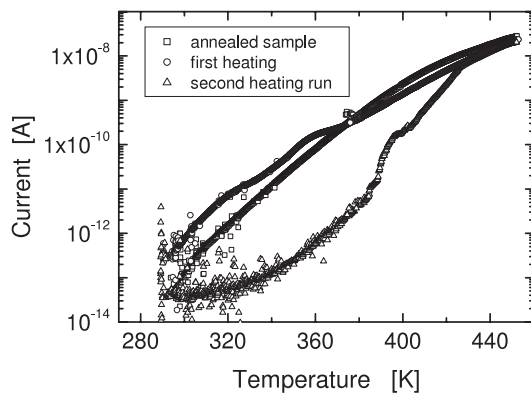


Figure 3. Current thermograms of the PDMS ferromagnetic gel recorded during heating.

VSM measurements the relaxation time of the magnetization process was determined as $\tau_N = 7.1$ ns. This means that the maximum energy dissipation ($\omega\tau_N = 1$) in the material studied is expected to be at the magnetic field frequency of $f \approx 22.5$ MHz.

The electrical conductivity was evaluated on the basis of the current measurements recorded during subsequent heating runs for the sample placed under a dc electric field. The data for the first, second and sixth heating runs are shown in figure 3, whereas results recorded for the respective cooling runs of the PDMS ferromagnetic gel are shown in figure 4.

The data recorded for the sixth heating run of the PDMS gel, in all figures, were called ‘annealed sample’ data. Measured current intensity varied from 0.5×10^{-13} to 0.5×10^{-8} A. A study of the current–temperature dependence revealed two ranges of different behaviours. The first, up to the temperature of 380 K, was for a weak increase in current and the second, over 380 K, was for a vigorous increase in current. A hump observed at 380–410 K was eliminated during subsequent heating runs. During cooling, two flexion points were observed. The first, initially at 390 K, moved its position to 400 K during repeated heating runs; the second, initially at 420–425 K, moved to 435 K.

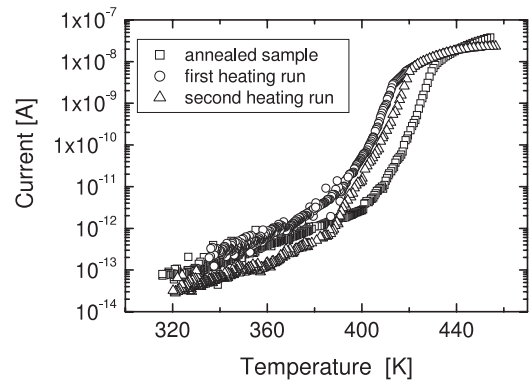


Figure 4. Current thermograms of the PDMS gel recorded during cooling.

The values of electrical conductivity σ were calculated by using the following equation:

$$\sigma = A^{-1}dU^{-1}I, \quad (6)$$

where A is the cross-sectional area of the measured surface, d is the thickness of the sample in the direction of measurement, U is the voltage applied to the sample, and I is the measured current intensity [16]. Electrical conductivity increased during heating from 2×10^{-12} S m⁻¹ to 2×10^{-8} S m⁻¹. The relative error of the electrical conductivity measurements was less than $\pm 5\%$.

The electrical conductivity determined was higher than that of pure PDMS as reported in the literature: 2.5×10^{-12} S m⁻¹ at room temperature [17] and 10^{-12} S m⁻¹ at 473 K [18]. The difference was probably caused by the dopant—magnetite—which has electrical conductivity of 25×10^3 S m⁻¹ at room temperature [19]. However, 0.6% addition of magnetite is too small to cause the increase in electrical conductivity of PDMS ferrogel due to percolation, which has the theoretical threshold of about 33% [5].

The irregularities and nonlinearities in the current thermograms shown in figures 3 and 4 for the first and second heating runs could be explained by the complex structure of the material studied. Because the PDMS ferromagnetic gel shows no phase transition at the applied temperatures [20], the hump recorded in the temperature range of about 330–380 K probably corresponded to the melting point of the palmitic acid (used as a surfactant preventing agglomeration of magnetic particles), which is located in the temperature range of 334–337 K [21], and the evaporation of water. Therefore, the observed changes in current thermograms between subsequent heating runs would indicate that each heating run caused gradual liberation of water and palmitic acid chemisorbed during preparation of the ferrogel. Also the vigorous heating of the PDMS samples could lead to the saturation of cross-linking and the stabilization of electrical properties of the PDMS ferrogel. This would lead eventually to a monotonic increase of the current with temperature. The flexion points recorded during cooling were probably due to the change in cooling rate.

On the basis of electrical conductivity measurements the activation energy E_A of the charge conduction process for the

Table 1. Activation energy E_A (in kJ mol^{-1}) of the charge transportation process in the PDMS ferromagnetic gel in different temperature ranges ΔT (in K).

	First heating run	Second heating run			Sixth heating run (annealed samples)	
ΔT	320–460	320–380	400–430	430–460	310–405	420–450
E_A	75 ± 5	80 ± 5	190 ± 10	75 ± 5	86 ± 5	57 ± 5

PDMS ferromagnetic gel could be determined according to the following formula [16]:

$$\sigma(T) = \sigma_0 \exp\left(\frac{E_A}{k_B T}\right), \quad (7)$$

where σ is the electrical conductivity, T is the temperature, and k_B is Boltzmann's constant. The activation energy was calculated using an Arrhenius plot of the form [22]

$$\ln(\sigma) = f\left(\frac{1}{T}\right) \quad (8)$$

in the regions of its linearity.

The activation energies, E_A , with the temperature ranges, ΔT , in which they were determined are listed in table 1. The activation energy values were lower than 260 kJ mol^{-1} , indicating that the process of electrical conduction was not connected to the charge carriers injected from the electrodes [23]. The first heating run showed the linearity of the electrical conductivity with temperature in the region 320–460 K and the activation energy of the nonannealed sample was found to be $75 \pm 5 \text{ kJ mol}^{-1}$. Despite the stable thermal properties of the PDMS ferromagnetic gel in the temperature range studied [20], the second heating run revealed three temperature subranges of linearity of the electrical conductivity: 320–380 K, 400–430 K and 430–460 K. For subsequent heating runs (up to the sixth heating run), two subranges of linearity of the electrical conductivity were always found in the following ranges of temperature: 310–405 K and 420–450 K. The activation energy showed an increasing tendency to a value of $86 \pm 5 \text{ kJ mol}^{-1}$ in the temperature range of 310–405 K and a decreasing tendency to a value of $57 \pm 5 \text{ kJ mol}^{-1}$ in the temperature range of 420–450 K. The change in the activation energy could be explained either by the participation of another type of charge carrier in the charge transportation process or by the higher degree of cross-linking which facilitated this process. However, this hypothesis needs further studies as the mechanism which caused the appearance of two subranges of linearity of the electrical conductivity with temperature described above is as yet unknown.

5. Conclusions

A study of the influence of temperature on the electrical conductivity of PDMS ferromagnetic gel was presented. During the heating of the PDMS in the temperature range of 295–460 K the electrical conductivity increased from about $2 \times 10^{-12} \text{ S m}^{-1}$ to $2 \times 10^{-8} \text{ S m}^{-1}$. The results obtained allowed us to conclude that the subsequent heating runs led to the liberation of the palmitic acid used as a surfactant in the

ferromagnetic gel studied. Also it seems that the residual water was liberated as well. The appearance of two subranges of linear increase of the electrical conductivity with temperature could be explained either by the liberation of two different types of charge carrier or by the increased degree of cross-linking. In the upper temperature subrange both types of charge carrier contribute to the conduction process. Because of the small mean diameter of the magnetite particles ($\langle x \rangle = 8.87 \text{ nm}$) and because of movements of ferromagnetic particles being restricted by the gel lattice ($\tau_B \rightarrow \infty$), PDMS ferrogel is magnetized mainly according to the Néel mechanism.

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