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Research articles

Enhanced specific loss power from Resovist® achieved by aligning magnetic easy axes of nanoparticles for hyperthermia

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A B S T R A C T

In this study, we precisely calculated the specific loss powers (SLPs) of magnetic nanoparticles (MNPs) based on dynamic hysteresis measurements. The advantage of this evaluation method is that the intensity and frequency of the applied magnetic field can be varied over a wide range for samples of various condition. The results show that the coercive field and SLP of Resovist® increase by orienting the magnetic easy axes of the nanoparticles. The magnetic field was applied either parallel or perpendicular to the nanoparticle orientation. The area enclosed by the dynamic hysteresis curve was larger when the AC field was applied parallel to the nanoparticle orientation, indicating a greater increase in the hyperthermia temperature. This characteristic originated from the magnetic anisotropy energy of the nanoparticles and is in good agreement with our simulational results. The SLP of a solid sample with an aligned easy axis measured under an AC field of 4 kA/m, which was applied parallel to the axis, was more than two times that of a liquid sample. We also evaluated the SLPs of superparamagnetic 4-nm-diameter γ-Fe_2O_3 and ferromagnetic 20–30-nm-diameter Fe_3O_4 MNPs and compared them to that of Resovist®.

1. Introduction

Magnetic nanoparticles (MNPs) are widely applied to biomedical applications such as magnetic fluid hyperthermia (MFH) [1], magnetic particle imaging (MPI) [2], and drug delivery systems (DDSs) [3]. They are also attracting much attention as theranostics agents, which means that treatment and diagnosis can be performed in a single system [4,5]. A commercially available MNP, called Resovist® (FUJIFILM RI Pharma), is a contrast agent for magnetic resonance imaging (MRI). It is also widely used for research on MFH [6] and MPI [7]. The specific loss power (SLP), which is also called specific absorption rate (SAR), indicates the amount of heat generated by the MNPs for MFH. In the conventional study, it is revealed that the heating performance is determined by the size, anisotropy, and saturation magnetization as the parameter of MNPs, the dosage of MNPs in tumor, and the condition of the applied field such as the field intensity and frequency [8]. The estimation of the SLP considering the volume of the target tumor is also important for the clinical efficacy [9]. To achieve a high SLP, the magnetic properties of Resovist® need to be investigated, and optimal conditions related to the applied field and the parameters of Resovist® should be determined. In this study, we fabricated samples of Resovist® with oriented easy axes [10,11] and measured their magnetic properties. The orientation of the easy axes should be considered for MFH applications wherein an AC magnetic field is employed for diagnosis. Moreover, it is important to clarify the magnetic properties of MNPs under an AC field in terms of the degree of anisotropy. In this study, we obtained the magnetization curves for Resovist® with oriented easy axes under an AC magnetic field with a frequency in the range of 1–100 kHz, considering their relaxation properties.

The energy of MNPs under an external magnetic field can be divided into two parts: anisotropy energy and energy associated with the external magnetic field [12]. When an AC magnetic field is applied to MNPs, a magnetic relaxation occurs because of the delay in the magnetization of the magnetic field. The Néel relaxation time τ_N and the Brownian relaxation time τ_B can be derived from the rotation of the magnetic moment and the rotation of the magnetic particles, respectively. The Néel relaxation time can be expressed as follows.

$$\tau_N = \tau_0 \exp\left(\frac{K_u V_M}{k_B T}\right) \tag{1}$$

where τ_0, T, and k_B denote the attempt time, temperature, and

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Boltzmann constant, respectively [13,14]. If Brownian relaxation and Néel relaxation occur simultaneously, the effective relaxation time τ_{eff} for the MNPs can be expressed as follows.

$$\tau_{eff} = \left(\frac{1}{\tau_B} + \frac{1}{\tau_N}\right)^{-1} \tag{2}$$

However, according to Eq. (2), Néel relaxation largely decides the effective relaxation time for particles with a small core size [15], though Brownian relaxation has been experimentally observed [16]. The relaxation time of an effective magnetic relaxation cannot be simply obtained using Eq. (2). In contrast to the conventional theory of the effective relaxation, the Brownian relaxation superimposed to the Néel relaxation was observed [17]. The dynamics of the easy axis derived from the Brownian relaxation was numerically and empirically observed [18,19]. Moreover, the Brownian relaxation occurred after the Néel relaxation was clearly detected by applying a pulse field in the transitional response of the magnetization and easy axis [20].

The magnetic relaxations generate thermal energy. The method of calculating the SLP by the calorimetric measurement has been reported [21]. The SLP is principally derived by the time change rate of temperature when magnetic field is applied [22]. In this study, we show that the SLP can be accurately calculated based on dynamic hysteresis measurements. It has also been reported that the calculated SLP values depend on the method of analyzing the temperature rise curve and on the shape of the sample even when the same particle and excitation condition are used [23]. However, the method of estimating the SLP from the AC hysteresis curve can eliminate the difficulties associated with measuring the temperature [24,25]. This evaluation method is expected to accurately determine the SLP values. Moreover, the SLP of MNPs inside living cells was estimated from the measurement of the AC magnetization curves [26,27]. Further, we discussed ways of increasing the SLP and the hyperthermia temperature. The obtained results are essentially different from those of hyperthermia experiments conducted under an applied AC magnetic field superimposed by a DC one, in which case the SLP reduces.

2. Materials and methods

2.1. Materials

Resovist® (commercially distributed by FUJIFILM RI Pharma) is γ-Fe_2O_3 particles, which have a core size in the range of 5–10 nm [18], and a hydrodynamic size of 75 nm measured by dynamic light scattering for the coated with carboxydextran in water. It is not only used as a contrast agent in MRI but also as a tracer of MPI [7] and a heating source for hyperthermia [6]. Although Resovist® exhibits superparamagnetism owing to its small core particle diameter, it has been reported that multicore particles effectively behave as a single particle [28] with a wide particle size distribution [29].

Fig. 1 shows the preparation processes of the liquid and solid samples. Two types of solid samples were prepared for Resovist®. The solution of 15 μl of undiluted Resovist® with concentration of 28 mg-Fe/ml was dispersed into purified water or epoxy for preparing the liquid or solid sample of 0.2 ml, respectively. For the solid sample, the MNPs were mixed with the epoxy bond (CEMEDINE Co.). The epoxy consisted of epoxy resin (viscosity of 100.0 Pa·s at 23 °C, density of 1.14 mg/mm^3) and polyamide (viscosity of 50.0 Pa·s at 23 °C, density of 0.99 mg/mm^3) at a volume ratio of 1:1. It turned to a solid state for 6 h after agitation for 5 min. The first sample contains MNPs held together using an epoxy bond in the absence of magnetic field, whereas the other sample contains MNPs under a DC magnetic field applied using an electromagnet for 8 h. Accordingly, the easy axes of the MNPs in the first sample are randomly oriented, whereas the easy axes of the MNPs in the second sample are aligned in a particular direction. The first sample is called as the random sample. For the second sample with an aligned easy axis, the DC and AC measurements were taken by applying a magnetic field parallel and perpendicular to the easy axis; the samples thus obtained are called the easy axis sample and the hard axis sample, respectively. Fig. 1(a–d) shows the samples for experiment. The intensity of the DC field during the preparation of the samples with aligned easy axes was 575 kA/m [11].

Liquid, random and oriented solid samples were also prepared, similar to the Resovist® samples, using superparamagnetic 4-nm-diameter γ-Fe_2O_3 and ferromagnetic 20–30-nm-diameter Fe_3O_4 MNPs [11] to compare their properties with those of Resovist® of various sizes of multi-core particles. The water-dispersed γ-Fe_2O_3 nanoparticles with core diameters of 4 nm supplied from Meito Sanyo Co. Ltd. were used. They were coated with carboxymethyl-diethylaminoethyl dextran. Furthermore, the Fe_3O_4 nanoparticles with diameters of 20–30 nm purchased from Nanostructured and Amorphous Materials Inc. were used. They were coated with polyethylenimine. The primary concentrations of γ-Fe_2O_3 and Fe_3O_4 nanoparticles dispersed in purified water were 28 mg-Fe/mL and 3 mg-Fe/mL, respectively. The concentrations of the MNPs in all the samples used in this study were adjusted to 2 mg-Fe/ml.

2.2. Magnetization measurements

The DC magnetization curves were obtained using a vibrating sample magnetometer (VSM, TOEI KOGYO, VSM-5), and the AC magnetization curves were obtained at a frequency in the range of 1–100 kHz under applied field amplitudes of 4 and 16 kA/m using homemade AC magnetization device equipped with a 210-turn water-cooled solenoid coil with a diameter of 16.0 mm for excitation. The measurements were taken at a temperature of 298 K. A magnetic field intensity of 16 kA/m was adopted as a typical value range of the magnetic field for hyperthermia. The magnetic properties were also investigated under applied field intensity of 4 kA/m, which is easily achieved for body-size excitation and excitation at higher frequency. The saturation magnetizations of the samples were estimated by fitting the DC magnetization curve at a field intensity of 800 kA/m to plot the magnetization curve using the Langevin function. The same plastic tube was used as the sample holder for both liquid and solid samples. The diamagnetism of the sample holder, and water or epoxy bond was calibrated in the VSM measurement. The SLP was quantified by calculating the area of the AC hysteresis curve as the magnetic loss, including the magnetization relaxation loss. Just one AC hysteresis curve was used to calculate one value of the SLP. The intrinsic loss power (ILP) was derived by the equation: $ILP = SLP/H^2 \cdot f$, where H and f are the intensity and frequency of the applied AC excitation field, respectively [30].

3. Results and discussion

3.1. DC magnetization curves

Fig. 2 shows the DC magnetization curves of four samples at a field intensity of 800 kA/m. The magnetization is normalized using the saturation magnetization and is represented in the unit of M/M_s. When a magnetic field of 575 kA/m is employed in the fabrication of an oriented sample, the magnetization of the liquid sample is fully saturated. In addition, the magnetization of the randomly oriented sample is 0.96 M/M_s, indicating that the magnetization is sufficiently aligned in the direction of the exciting magnetic field at the time of orientation after solidification, though some particles that cannot be partially oriented are present. From the DC magnetization curve, the saturation magnetization of Resovist® was obtained as 94.4 A·m^2/kg-Fe. Fig. 3 shows the DC magnetization curves of the samples at field intensities of 4 and 16 kA/m. First, it is confirmed that the liquid sample does not exhibit a coercive field and remanent magnetization. As particles in the liquid sample rotate after DC or low frequency field has been applied,

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