INFLUENCE OF SATURATION MAGNETIZATION AND VISCOSITY ON SPECIFIC LOSS POWER FOR CoFe$_2$O$_4$ AND MnFe$_2$O$_4$ MAGNETIC NANOPARTICLES

Luu Huu Nguyen$^{1,2,*}$, Phan Quoc Thong$^{1,2}$, Pham Hong Nam$^2$, Le Thi Hong Phong$^2$, Pham Thanh Phong$^1$, Nguyen Xuan Phuc$^2$

$^1$University of Khanh Hoa, 01 Nguyen Chanh Road, Nha Trang, Khanh Hoa
$^2$Institute of Materials Science, VAST, 18 Hoang Quoc Viet Road, Cau Giay, Ha Noi

*Email: lhnohh2@gmail.com

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ABSTRACT

Magnetic nanoparticles absorb energy from external alternating magnetic field to create a nanosized heating source. Specific loss power (SLP) is affected strongly by several magnetic parameters of material and viscosity of nanofluid. In this study, the specific loss power as dependent on saturation magnetization was calculated for hard ferrite CoFe$_2$O$_4$ ($K = 290$ kJ/m$^3$) and soft ferrite MnFe$_2$O$_4$ ($K = 3$ kJ/m$^3$) with two values of viscosity in biological range 1-2 mPas. Besides, we investigated the experimental dependence SLP on their saturation magnetization while changing viscosity using agar powder. A large change of slope $\frac{SLP}{M_s}$ was found for CFO when the viscosity changes; whereas it remained almost unaffected by the variation of viscosity fluid of MFO. All calculation and experimental results are discussed via the competition between Néel and Brown relaxation.

Keywords: Neel-Brown relaxation, saturation magnetization, specific loss power, viscosity.

1. INTRODUCTION

Magnetic nanoparticles (MNPs) have recently been the subject of intensive study of both basic research and applications; especially in biomedicine and biotechnology [1 - 6]. Magnetic Inductive Heating (MIH) is the phenomenon that MNPs adsorb energy from external alternating magnetic field (AMF) to create a heating source that can be used as thermo seed in ‘killing’ cancer cells in hyperthermia [2, 5 - 7]. The so-called specific loss power (SLP) is commonly used to describe the MIH capacitance or the ability to absorb energy from AMF of the MNPs. In MIH, there are several mechanisms of energy loss that could contribute to the SLP: hysteresis loss, Brown relaxation, and Néel relaxation [1, 4, 6, 8]. For superparamagnetic nanoparticles, it is generally accepted that the major heating contribution is based on Néel relaxation and Brown relaxation. The Néel-Brown SLP depends on particle size ($D$), size distribution ($\sigma$), saturation
magnetization \( (M_s) \), magnetic anisotropy constant \( (K) \) and the viscosity of magnetic fluid \( (\eta) \) [6, 9, 14]. Rosenweig [6] indicated the different influence of viscosity on SLP of Fe\(_2\)O\(_4\) nanoparticles \( (K = 23 - 41 \text{ kJ/m}^3) \) and CoFe\(_2\)O\(_4\) \( (K = 180 - 200 \text{ kJ/m}^3) \) nanoparticles. This, in fact, is a theoretical evidence shown for the competition between Néel and Brown relaxation in SLP. Surprisingly, there has been very few experimental reports on the influence of viscosity on the SLP, especially in the biological range of 1 mPas – 2.12 mPas. Jeun et. al. investigated the effect of viscosity on SLP of Co-nanofluid and Fe-nanofluid and indicated no such a dependence for both the materials [11]. Besides, Fortin et al. found that SLP decreased with increasing viscosity for \( \gamma - \text{Fe}_2\text{O}_3 \) and CoFe\(_2\)O\(_4\) [12, 13]. Recently, Pineiro-Redondo et al. reported that only a very slight SAR increase from 36.5 to 37.3 W/g takes place as the solvent viscosity increases from 1 mPas (water) to 17 mPas (ethylene glycol) for PAA-coated magnetite ferrofluids [14]. It is important to note that the impact of the anisotropy constant \( (K) \) to SLP was not taken into attention by any of these reports [11 - 14]. On the other hand, SLP depends strongly on saturation magnetization \( (M_s) \). Although it is generally accepted that SLP increases as a power function of \( M_s \) \( (\text{SLP} \propto M_s^n \text{ with } n>0) \), there is still controversy of whether \( \alpha = 1 \) \( (\text{i.e., linear function}) [15] \) or \( \alpha = 2 \) \( (\text{i.e., quadratic function}) [8, 16] \). Moreover, the considerations of dependence SLP on \( M_s \) in all those works [8, 15, 16] were done with the assumption that the viscosity of nanofluid unchanged. Thus, a practical question naturally arises such that how would the dependence SLP vs \( M_s \) be affected by the viscosity of nanofluid and would it be as a rule common to various magnetic materials; these need to be considered.

In the present work, we calculate the dependence of SLP on the saturation magnetization \( (M_s) \) with various viscosities in biological range for CoFe\(_2\)O\(_4\) (CFO) and MnFe\(_2\)O\(_4\) (MFO) nanofluids. CFO and MFO nanoparticles were used as core particles each to be coated with various amounts of the polymer to creating two sample series with various saturation magnetization of similar magnetic anisotropy constant. The experimental results of the SLP depending on \( M_s \) was discussed and compared with calculation behaviour. As will be shown by either experimental and theoretical results, the SLP versus \( M_s \) is effect clearly by the viscosity of magnetic fluid \( (\eta) \) and quite differently for hard (high K) and soft (low K) magnetic ferrite materials.

2. EXPERIMENTAL

CFO and MFO nanoparticles were synthesized by hydrothermal method, Alginate coating was performed following the procedure described in [17]. For each of CFO and MFO, five ratios of shell-to-core concentration of 0 %, 8,3 %, 16,7 %, 25 %, 33,3 % were used, so that the two series of the coated samples denoted correspondingly as: CFO-S\(_i\) and MFO-S\(_j\); \( i = 1 - 5 \) were fabricated. These obtained vacuum dried nanoparticles were then ultrasonically dispersed in water to form nanofluids of concentration of 6 mg/ml. Finally, agar powder with appropriate amount was added for each CFO-S\(_i\) and MFO-S\(_j\) nanofluid to fabricate research specimens of viscosity of 1 mPas and 2 mPas. The crystalline structure were determined by X-ray diffraction (XRD) using equipment Siemens D-5000. The magnetic properties of the magnetic nanoparticle powder were measured by a homemade vibrating sample magnetometer (VSM). The hydrodynamic diameter \( (D_{h0}) \) of the nanofluids of CFO and MFO nanoparticles was characterized using a dynamic light scattering (DLS) system. All the MIH experiments were carried out on the set up with the use of a commercial generator (RDO HFI 5 kW) providing an alternating magnetic field of amplitude 65 Oe, and frequency of 178 kHz.
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3. RESULTS AND DISCUSSIONS

The XRD patterns of uncoated CFO and MFO powder, presented in Figure 1, indicate that the samples are of single phase.

As can be seen in Figure 2, the uncoated CFO and MFO nanofluids had average $D_H = 25.2$ and 21.4, respectively with a narrow size distribution, $\sigma = 0.18$.

Magnetization hysteresis curves measured at room temperature of all the CFO and MFO coated samples are presented in Figure 3. As expected, the saturation magnetization of the coated nanoparticles decreases clearly with increasing the polymer concentration from 0 to 33.3%; namely it decreases from 77.3 emu/g to 59.8 emu/g and from 72.4 emu/g to 62.9 emu/g, for CFO and MFO specimen, respectively (Table 1).

![Figure 1. XRD patterns for (a) CFO and (b) MFO nanoparticles.](image)

![Figure 2. Dynamic size distributions of (a) uncoated CFO and (b) MFO nanoparticles fluids ($\eta$=1mPa.s²). The solid lines represent the fitting curve assuming the log-normal function.](image)

![Figure 4. Dependence of SLP on $M_s$ for CFO and MFO ferrofluids of viscosities of 1 mPas and 2 mPas.](image)

We, then, calculated the relaxation times and the specific loss power for CFO and MFO nanoparticles with corresponding diameter of 25.2 nm and 21.4 nm, and their nanofluids with the two viscosity values. The calculations were conducted with use of the field amplitude of $H_o = 65$ Oe and the frequency $f = 178$ kHz, that the $H_o f$ product is in the region of biological limit ($H_o f < 4.85 \times 10^8$ Am$^{-1}$s$^{-1}$ [18]). We assumed magnetic anisotropy ($K$) equal to the quantity obtained for bulk materials (Table 1). The contribution of hysteresis loss to SLP of CFO nanofluid can be negligible because all the MIH experiments were performed in a small field amplitude, i.e. of 65 Oe [11]. And, because the MFO nanoparticles used were superparamagnetic nanoparticles of soft ferrite, the major heating contributions for MFO are those based on the Néel relaxation and the Brown relaxation.
Therefore, our loss power calculations deal with those relaxation contributions for both the materials. Besides, the surface layer of samples was 1 - 2 nm – smaller than size nanoparticles.

Table 1. Materials parameters of samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D (nm)</th>
<th>σ</th>
<th>M_s (emu/g)</th>
<th>K (kJ/m^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFO-S1</td>
<td>25.2</td>
<td>0.18</td>
<td>77.4</td>
<td>290</td>
</tr>
<tr>
<td>CFO-S2</td>
<td>21.4</td>
<td>0.18</td>
<td>64.7</td>
<td>67.5</td>
</tr>
<tr>
<td>CFO-S3</td>
<td>66.1</td>
<td>0.18</td>
<td>61.9</td>
<td>65.8</td>
</tr>
<tr>
<td>CFO-S4</td>
<td>59.8</td>
<td>0.18</td>
<td>64.7</td>
<td>68.1</td>
</tr>
<tr>
<td>CFO-S5</td>
<td>61.9</td>
<td>0.18</td>
<td>64.7</td>
<td>65.8</td>
</tr>
</tbody>
</table>

The specific loss power $SLP$ (W/g) was described as [6]:

$$SLP = \frac{P}{\phi \rho}$$

where $\phi$ is the volume fraction, $\rho$ is the mean mass density of the nanoparticles and $P$ (loss power density) is described as [6,7]:

$$P = \pi \mu_0 H_0^2 \chi \frac{2\pi f \tau}{1 + 2\pi f \tau^2}$$

where $\mu_0$ is the permeability of free space; $H_0$ and $f$ are the amplitude and the field frequency of AMF; $\chi$ is the equilibrium susceptibility; and $\tau$ is the effective relaxation time. The equilibrium susceptibility and the effective relaxation time was presented in [6, 7, 18]. Besides, $SLP$ depends strongly on size distribution, and its distribution [6, 12], so, we followed those reports to perform the calculation taking into account the mean particle sizes $D$ of 25.2 nm and 21.4 nm for CFO and MFO, respectively and the same distribution deviation of 0.18. The calculation specific loss power $SLP_{cal}$ of samples CFO and MFO with various saturation magnetization $M_s$ in two viscosities (1 mPas and 2 mPas) are shown in Figure 4.

Based on calculation results, $SLP_{cal}$ was an increasing linear function of $M_s$; This tendency agrees with Lee et al. [15]. The slope $\frac{SLP_{cal}}{M_s}$ obtained for CFO was 0.45 and 0.23 W/emu for the ferrofluid with viscosity of 1 mPas and 2 mPas, respectively. The slope $\frac{SLP_{cal}}{M_s}$ obtained for
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MFO, however, remains almost unchanged when the viscosity of nanofluid changed from 1 mPas to 2 mPas; namely it was 0.29 W/emu. Theses calculation results will be compared with their experimental results in the following section.

Heating curves measured at the field amplitude of $H_o = 65$ Oe and the frequency $f = 178$ kHz for all the ferrofluid samples with core material of CFO and MFO are presented on Figure 5 and Figure 6, respectively. The experimental $SLP$ was described as [5, 10, 12]:

$$SLP_{exp} = C \frac{m_s \Delta T}{m_i \Delta t} \quad (3)$$

Figure 5. Magnetic heating curves measured for CFO nanofluids with various magnetizations, and viscosity of 1mPas (left), and 2 mPas (right).

The experimental $SLP_{exp}$ values are gathered in Table 2. These results indicate that $SLP_{cal}$ is an increasing linear function of $M_s$ ($R^2 > 0.93$), which agrees well with the results reported by Lee et al. [15].

Figure 6. Magnetic heating curves measured for MFO nanofluids with various magnetizations, and viscosity of 1mPas (left), and 2 mPas (right).

Moreover, while a clear decrease in both $SLP_{cal}$ and $SLP_{exp}$ when the viscosity increases from 1 mPas to 2 mPas was observed for CFO material; with the case of MFO, however, the $SLP_{cal}$ and $SLP_{exp}$ are almost unaffected by the viscosity variation (Table 1 and Table 2). The observed behaviour that the heating loss power $SLP$ is effected by viscosity for the case of hard ferrite and unaffected for soft ferrite is a result of the competition between the Néel and the Brown relaxation. Namely, because viscosity is involved in the Brown relaxation term, so for materials with high enough K value (like CFO) this term becomes nominating over that of the Neel relaxation. And, the $SLP_{exp}$ and $SLP_{cal}$ of MFO (low K) nearly remains unchanged (change of less than 5 % for samples MFO-S, $i = 1 - 5$), which means that the Néel relaxation term then dominates.
The slope $\frac{SLP_{exp}}{M_s}$ obtained for CFO is 0.44 and 0.57 W/emu, respectively for the 1mPas and 2 mPas viscosity. Whereas for MFO, the slope $\frac{SLP_{exp}}{M_s}$ = 0.56 W/emu and unchanges when the viscosity varies from 1 mPas to 2 mPas.

Table 2. The value of $SLP_{exp}$ for samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>CFO</th>
<th>MFO</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>31.3</td>
<td>31.3</td>
</tr>
<tr>
<td>S2</td>
<td>27.7</td>
<td>27.7</td>
</tr>
<tr>
<td>S3</td>
<td>27.5</td>
<td>26.5</td>
</tr>
<tr>
<td>S4</td>
<td>23.9</td>
<td>23.6</td>
</tr>
<tr>
<td>S5</td>
<td>23.5</td>
<td>20.3</td>
</tr>
</tbody>
</table>

These results agree well with theoretical results reported in Ref. [6, 12, 13] when the SLP depend on the viscosity of nanofluid for magnetic materials with the value of $K$ is high. It is important to note that, although Jeun et. al. remarked on no dependence of SLP on the viscosity, one still can note in Fig. 4 of this report [11] some change of heating rate of Co-nanofluid with viscosity changing. The difference of impact of the viscosity to the calculation $SLP$ indicates the competition between the Néel and the Brown relaxation. These results explain the fact that the main differences between the performance of the resultant nanofluids are due to the anisotropy constants. The competition between the Néel and the Brown relaxation is expressed via the Brown relaxation time, the Néel relaxation time and the effective relaxation time [6, 17]. Both Brown and Néel relaxation times depend on particle size, whereas only the Brown relaxation time depends on the viscosity [14, 18] and only the Néel relaxation time depends on $K$ [6]. Deatsch et al. indicated that the Brownian relaxation time became significant only for particle diameter is above 20 nm for the case of Fe$_3$O$_4$ when taking $K = 10$ J/m$^3$ [18].

As one can easily realize, there is still a rather large difference between the calculation slope, $\frac{SLP_{calc}}{M_s}$ and that determined experimentally, $\frac{SLP_{exp}}{M_s}$. For the case of MFO, when the viscosity increased from 1 mPas to 2 mPas, $\frac{SLP_{exp}}{M_s} = 0.56$ W/emu while $\frac{SLP_{calc}}{M_s} = 0.29$ W/emu.

For CFO, the experimental slope $\frac{SLP_{exp}}{M_s}$ increases from 0.45 W/emu to 0.57 W/emu; while the calculation slope $\frac{SLP_{calc}}{M_s}$ decreases from 0.45 W/emu to 0.23 W/emu when the viscosity increased form 1 mPas to 2 mPas. We assume the disagreement might be related with the effect of aggregation, agglomerating of nanoparticles in nanofluids. The aggregation of MNPs could induce an increase or decrease of $M_s$ or $K$ that results in affecting the value of $SLP$. And, an aggregation of MNPs can also induce an increase of the hydrodynamic diameter - the Brown relaxation time increasing – resulting in an increase or decrease of $SLP$ [18]. If the hydrodynamic diameter increases twice by the aggregation of MNPs, the Brownian relaxation time will increase eightfold (Eq. (4) [6, 7]) so the $SLP$ would change very much.
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\[ \tau = \frac{3\eta V_B}{k_B T} \]  \hspace{1cm} (4)

On the other side, the agglomerating of MNPs can induce also magnetic interactions between nanoparticles, resulting in certain conditions in a decrease of hyperthermia efficiency. These results were found in theoretical and experimental works at biomedical applications [21 - 25]. So all the considerations have indicated the competition between the Néel and the Brown relaxation depending on the viscosity ($\eta$) and the magnetic anisotropy ($K$). Yet, one needs more studies for influence of aggregation, agglomerating of nanoparticles, surface layer of MNPs on SLP in MIH.

4. CONCLUSION

In summary, the competition of the Néel and Brown relaxation loss results showed interesting dependences on both particle intrinsic properties as well as the viscosity of its environment. SLP was an increasing linear function of $M_s$. However, all the slope $\frac{SLP}{M_s}$ of CFO changed when the viscosity changed and all the slope $\frac{SLP}{M_s}$ of MFO almost unchanged with changing of viscosity. For the hard ferrite nanoparticles (CFO) the SLP decreased strongly with increasing the viscosity, whereas these characteristic quantities remain almost not changed for the case of soft nanoparticles (MFO). All results - the influence of the viscosity on SLP for hard and soft ferrite, was important for oriented manufacturing magnetic materials in MIH.

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Influence of saturation magnetization and viscosity on specific loss power for CoFe₂O₄ and MnFe₂O₄ nanocomposites. 


TÓM TÁT

ÁNH HƯỞNG CỦA TỮ ĐÔ BẢO HÒA VÀ ĐỘ NHỚT ĐẾN CÔNG SUẤT ĐỘT TỪ CỦA HẢI HỆ HẠT NANO TỪ CoFe₂O₄ VÀ MnFe₂O₄

Lưu Hữu Nguyên¹,², Phan Quốc Thông¹,², Phạm Hồng Nam⁴, Lê Thị Hồng Phong⁴, Phạm Thanh Phong¹, Nguyễn Xuân Phúc²

¹Dai học Khánh Hòa, 01 Nguyễn Chánh, Nha Trang, Khánh Hòa
²Viện Khoa học và liệu, Viện Hàn lâm KHCNVN, 18 Hoàng Quốc Việt, Cầu Giấy, Hà Nội

Email: lhnohh2@gmail.com

Các hạt nano từ sê tro thành những nguồn nhiệt kích thước nano khi hấp thụ năng lượng từ từ trường xoay chuyển ở vùng tần số radio. Công suất đột tử phụ thuộc mạnh vào một số tham số từ tính cơ bản của vật liệu và độ nhớt của chất lỏng từ. Chúng tôi đã tính toán công suất đột tử, SLP, phụ thuộc vào độ bão hòa, Ms, của hải hết hạt nano từ có các giá trị di hướng từ rất khác nhau là: CoFe₂O₄ (K = 290 kJ/m³) và MnFe₂O₄ (K = 3 kJ/m³). Các phụ thuộc này cũng được tính cho 2 tham số độ nhớt ở biên vùng ứng dụng y sinh là 1 và 2 mPa.s. Đồng thời, chúng tôi khảo sát bằng thực nghiệm sự ảnh hưởng của từ độ bão hòa đến công suất đột tử cho 2 loại mẫu chất lỏng từ hệ hạt nano từ ferit nên Co và Mn nói trên với việc dùng agar thay đổi độ nhớt. Sự suy giảm SLP theo Ms, thay đổi khi đó nhớt thay đổi được tìm thấy đối với hệ chất lỏng CoFe₂O₄ trong khi đó, sự suy giảm SLP theo Ms, thay đổi với hệ MnFe₂O₄ gần như không phụ thuộc vào độ nhớt của chất lỏng từ. Các kết quả thí nghiệm và thực nghiệm được chứng tỏ khả năng đốt trong sự canh tranh giữa cơ thể tốn hao hơi phun Néel và tốn hao hơi phun Brown.

Từ khóa: công suất đột tử, độ nhớt, từ độ bão hòa, hơi phun Néel, hơi phun Brown.