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Improving heat generation of magnetic nanoparticles by pre-orientation of particles in a static three tesla magnetic field

Mathias M. Beck[a,*], Christian Lammel[a], Bernhard Gleich[b]

[a] Institute for Machine Tools and Industrial Management, Technical University of Munich, Boltzmannstr. 15, 85748 Garching, Germany
[b] Institute of Medical Engineering, Technical University of Munich, Boltzmannstr. 11, 85748 Garching, Germany

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ABSTRACT

Inductive heating of electrically insulating materials like fiberglass reinforced thermoplastics (FRTP) without susceptors is not possible. However, due to their low thermal conductivity a volumetric heat generation method is advisable to reach short heating times to melt this material for reshaping. This can be done with magnetic nanoparticles as susceptors within the thermoplastic of the FRTP using Néel relaxation. During the heating process the particle's magnetic moment rotates with the field while the particle itself is fixed within the thermoplastic. Therefore the heat dissipation of each particle depends on its orientation within the field. To achieve the maximum heat generation of the particles we pre-oriented the particles within a plastic at the best angle to the applied AC field for induction. To do this, five mass percent nanoparticles were dispersed in an epoxy resin, which was then hardened at room temperature in a static three Tesla magnetic field. After its solidification the heating behavior of the sample was compared to a reference sample, which was hardened without a field. The oriented particles showed an increased heating rate when oriented parallel to the applied AC field. The absorption rate was 3.3 times as high as the undirected reference sample. When the alternating electromagnetic field was perpendicular to the oriented particles, the specific absorption rate was similar to that of the reference sample. We compare this result with theory and with calculations from literature, and conduct a numerical simulation.

1. Introduction

Due to the increased use of lightweight materials in the area of mechanical engineering, especially aeronautical and automotive engineering, there is also an increased need of fast production methods for these materials [1]. Within this field reinforced thermoplastics, for example using fiberglass, have strong potential due to their reshapeability and better recyclability compared to thermoset components [2]. These thermoplastic materials are generally hot pressed during manufacturing, which is a fast process only for flat samples due to their low thermal conductivity that results in only small possible heat input through the surface of the components [3]. In order to form and reshape thermoplastic composites the duration and energy consumption of this process is a problem to address. Due to the high thermal conduction, thicker samples in particular can only be heated slowly as the temperature on the surface is limited by the degradation temperature of the thermoplastic. This makes it difficult to achieve a relevant production speed in commercial applications. Volumetric heating using magnetic nanoparticles as susceptor for inductive energy transfer is one possible way to overcome this constraint. Induction heating using nanoscale particles allows energy transfer into and volumetric heat generation within the particles. This avoids the heat transfer limit via the surface of the composite and therefore has a potential for increasing the production speed.

In general, there are two possible mechanisms regarding nanoparticle heating: Brown relaxation heating occurs due to frictional losses while the particle rotates in a fluid, Néel relaxation heating by rotation and fluctuation of the magnetic moment using the different energy levels due to the magnetic anisotropy of the particle [4]. Many studies are being conducted in the medical field, mainly with respect to Brown relaxation using ferrofluids [5–9], but only few studies have been conducted in the field of mechanical engineering regarding nanoparticle heating within solid matrices. Tay et al. [10] presented a proof of concept for rapid curing of bonds using inductively heated nanoparticles, and tested the resulting bonds for the reduction of strength due to the particles. He showed that nanoparticles are suitable for the demands of mechanical engineering. Temperature profiles concerning the reaction of resins and the energy absorption of ferritic particles were modeled by Ye et al. [11]. Miller et al. [12] heated epoxy resin in about 70 s over 100 °C using FeCo particles, a frequency of 26 kHz and

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* Corresponding author.
E-mail address: Mathias.Beck@tum.de (M.M. Beck).

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an electromagnetic field strength of 20.0 kA/m. These are parameters that are realistic for larger scale manufacturing, but still the heating rate is not high enough with respect to the production cycle times in automotive engineering of 60 s and the demanded temperature increase of about 250 °C up to the melting temperature of generally used thermoplastics such as polyamide. It follows that there is a need for large energy absorption of particles that are low in price and available in large amounts, a requirement which is hard to fulfill.

To achieve the full energy absorption/heat generation of particles that are dispersed in a solid material, we oriented magnetic nanoparticles parallel to the magnetic AC field. Since the energy absorption in such a system is dependent on the orientation of the particle with respect to the applied field, we have shown that with the help of this alignment the heat generation can be increased significantly.

2. Theory

The heating mechanism for an inductively heated particle is dominated by the relaxation mechanism that has the shorter time constant [13]. For Néel (τ_N) and Brown relaxation (τ_B), these relaxation times are given by:

$$\tau_N = \tau_0 exp\frac{KV_M}{k_B T} \tag{1}$$

$$\tau_B = \frac{3\eta V_H}{k_B T} \tag{2}$$

Where $\tau_O=10^{-9}$ s, K is the anisotropy constant, V_M the volume of the particle, k_B the Boltzmann constant, T the temperature, η the viscosity and V_H the hydrodynamic particle volume. The effective relaxation time results to

$$\frac{1}{\tau} = \frac{1}{\tau_B} + \frac{1}{\tau_N} \tag{3}$$

As the viscosity of solid materials is very high, Néel relaxation dominates the heating mechanism of magnetic nanoparticles with an electromagnetic AC field when fixed in a solid plastic. There the particles cannot move and only their magnetization rotates with the field. In this case, the amount of energy absorption by the particle, which is proportional to the heat generation, depends on the angle φ between the particle's easy axis and the external magnetic AC field (Fig. 1). If this angle is zero – meaning the particle's easy axis is aligned with respect to the electromagnetic AC field – the amount of energy absorption is maximized [4]. The magnetic field and magnetization are aligned with respect to the easy axis. In the general case, without any external force acting on the particles, they have a statistically random orientation in space. The aim of this work is to orient the particles in space so as to increase the energy absorption.

The remanence and coercivity of a randomly oriented particle system are both approximately half of the value of the oriented case [5,14]. This leads to a four times higher theoretical energy absorption of the aligned particles (φ=0) in a Stoner-Wohlfarth-model [15]. Briefly this model describes the mechanism of magnetic hysteresis and can be used for magnetic nanoparticles.

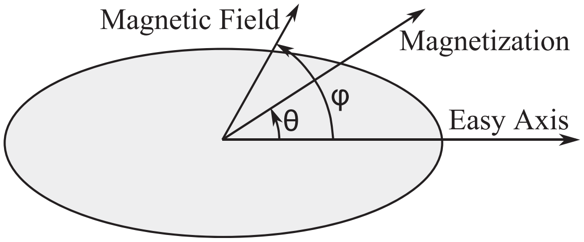

Fig. 1. Sketch of particle magnetization in magnetic field. If the external field is not aligned with the easy axis the magnetization of the particle rotates out of the energetic optimal axis. Therefore the maximal energy absorption cannot be reached.

The energy absorption in Néel relaxing systems is proportional to its hysteresis area [16]. A semi-analytical calculation, backed by numerical simulations, of hysteresis loops for the random oriented case is [4]

$$A(T) = 4 \quad M_S \mu_0 H_K (1 - \kappa^{0.5}) \tag{4}$$

and for the φ=0 case

$$A(T) = 0.96 \quad M_S \mu_0 H_K (1 - \kappa^{0.8}) \tag{5}$$

with the saturation magnetization M_S, the anisotropy field $\mu_O H_K$ and the factor κ defined as

$$\kappa = \frac{k_B T}{K_{eff} V} \ln\left(\frac{k_B T}{4 \quad \mu_0 H_{max} M_S V f \tau_0}\right) \tag{6}$$

with the Boltzmann constant k_B, the temperature T, the effective anisotropy K_{eff}, the volume V, the frequency factor of the Néel-Brown relaxation time τ_O, the frequency f and amplitude $\mu_O H_{max}$ of the electromagnetic AC field. When restricting the calculation to the hysteresis loops in the intermediate to high dissipation limit (κ~1, [17]) the influence of the exponents of κ disappears and the first factor of Eqs. 4 and 5 determines the different hysteresis areas. The hysteresis area of the aligned nanoparticles compared to the unaligned case is larger by the factor of 4/0.96=4.17. As the heat generation is proportional to the hysteresis area, it is expected to increase by the same factor when aligning the particles to the AC magnetic field.

3. Material and methods

3.1. Simulation

The simulation was conducted using the micro magnetic simulation package *NMAG-sim (University of Southampton, United Kingdom).* 400 evenly distributed spherical particles with a core diameter size of 20 nm were simulated, which is the upper value of the particles' nominal single diameter used in the experiment given in the datasheet. To achieve an ideal result, the distance between the particles was increased until all interactions between the particles vanished at 160 nm. The Landau-Lifshitz-Gilbert damping parameter was set to 0.1 and the exchange coupling to 2.1e-11 J/m. Three different simulations were conducted differing in the orientation of the particle's easy axis with respect to the applied field – parallel, perpendicular and randomly oriented.

3.2. Particles

Uncoated iron(II, III) oxide (Fe_3O_4) particles were purchased from *IoLiTec (Ionic Liquids Technologies GmbH, Germany)*. According to the data provided these particles had a nominal average particle size of 15–20 nm and a purity of at least 99.5%. These spherical particles were delivered as a powder which was then prepared.

3.3. Dynamic Light Scattering (DLS)

36.5 mg particles were put in a fluid of 2 ml H_2O and 1 ml 10 mM HNO_3. This dispersion was vortexed for five minutes and dispersed by ultrasound for 6 h. The size of the particles was measured with a Zetasizer NanoZS (*Malvern Instruments GmbH, Germany*).

3.4. Sample Preparation

The epoxy resin-hardener-combination "SR 1720/ SD 7840" (*Sicomin Epoxy Systems, France)* was used as matrix for the samples. First the particle-powder was stirred into the resin. The mixture was mingled using ultrasound pulses for 60 min while being constantly cooled in a water quench (120 W at 30 kHz with a duty cycle of 25%