The Effect Of Temperature On Magnetic Behavior Of Magnetite Nanoparticles And Its Nanocomposites

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Abstract. The magnetic properties of magnetite nanoparticles and magnetite-thermoplastic natural rubber (TPNR) nanocomposites was prepared by melt-blending method has been studied using vibrating sample magnetometer (VSM). The saturation magnetization (M_s), remanence (M_R), squareness (M_R/M_s), coercivity (H_c) and exchange-bias field (H_{eb}) for magnetite nanoparticles and its nanocomposites increased with decreasing temperature from 298 to 93 K. The increment of magnetization might be due to the decrease in thermal energy while the enhancement of coercivity and exchange-bias field is attributed to the exchange interaction at the interface between the ferrimagnetic (Fe₃O₄) and spin-glass-like surface layer on the nanocrystalline magnetite.

Keywords: Magnetic nanoparticles, Polymer nanocomposites, Coercivity, Exchange-bias PACS: 75.75.+a

INTRODUCTION

Nanosized magnetite (Fe₃O₄) is a member of spinel type ferrite. It is important in magnetic and used for recording material, pigments, electrophotographic developer, mineral separation, efficient heat transfer applications, cancer therapy, etc. [1]. It is also well known that magnetic properties exhibited by nanoparticles are different from those found under bulk conditions, and they are strongly dependent upon finite size effects. Such effects include changes in the average coordination number and the presence of uncompensated spins due to the breaking of symmetry at the boundaries. In this work, the temperature dependence of the magnetic properties of Fe₃O₄ nanoparticles and its nanocomposites were studied at our laboratory.

EXPERIMENTAL Materials

 Fe_3O_4 nanoparticles was supplied by Nanostructured & Amorphous Materials, Inc., USA. Natural rubber (NR) and polypropylene (PP) were supplied by Rubber Research Institute of Malaysia (RRIM) and Mobile (M) Sdn. Bhd., respectively. Liquid natural rubber (LNR) was prepared by the photosynthesized degradation of NR in visible light in our laboratory.

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Preparation of the Nanocomposites Samples

TPNR filled Fe_3O_4 nanocomposites with 4 to 12 weight percent of Fe_3O_4 were prepared by melt-blending technique using laboratory mixer (Model Thermo Haake 600p). The weight ratio of PP, NR and LNR is 70:20:10 with the LNR as the compatibilizer for the mixture.

Characterization

The specimens for the magnetic measurements were made into disc shape of 5 mm in diameter. The magnetic properties were measured by using a vibrating sample magnetometer (Model VSM 7404) from room temperature, 298 K to 93 K. The measurements were carried out in a maximum external field of 12 kOe. The external field was applied parallel to the sample.

RESULTS AND DISCUSSION

The typical temperature dependence of the saturation magnetization (M_s) and remanence (M_R) for Fe₃O₄ nanoparticles at applied field of 12 kOe is shown in Fig. 1. The saturation magnetization for Fe₃O₄ nanoparticles at room temperature (298 K) is 63.79 emu/g, which is lower than bulk Fe₃O₄ (92 emu/g) [2]. The reduction in saturation magnetization may be attributed to the surface disorder or spin canting at the particles surface [3]. In the temperature range of 93 to 298 K, both saturation magnetization and remanence increased with a decrease of temperature. This is typical behavior for ferromagnetic materials and can be considered as a result of the decrease in thermal energy [4].

In Fig. 2, the coercivity (H_c) and exchange bias field (H_{eb}) as a function of temperature is plotted for Fe₃O₄ nanoparticles. The exchange bias is represented by a shift in the magnetization hysteresis loop in the direction of the cooling field, and is generally defined as $H_{eb} = |H_{C1} + H_{C2}|/2$ [5]. It is evident that the coercivity increases as the temperature is decreased. It is also evident that the exchange bias field, the shift of the hysteresis loop, increases as the temperature decreases [5]. Obviously, there is a boundary at 173 K. The exchange bias field is almost zero when the temperature is greater than 173 K.

The physical origin of exchange bias is rather generally accepted to be the exchange coupling between the ferro or ferrimagnetic (FM) and antiferromagnetic (AFM) components at the interface. The increased in coercivity and the exchange bias field are the result of increased in AFM anisotropy energy barriers, K_{AFM} with decreasing temperature [6]. Although surface defects introduced by the synthesis techniques should certainly induce surface spin disorder, the change of coordination of the surface atoms, especially in oxides due to broken exchange bonds, can also render surface spin disorder. When this spin disorder freezes at low temperatures it can behave as a "spin glass like" layer at the surface of the nanoparticles. These spin glass surface layers can play the role as "AFM" in the case of FM or ferrimagnetic particles. Thus, in this case, 173 K is the "Neel temperature" for "spin glass like" layer which

acts as AFM and the net effect is an enhancement of coercivity and a shift of the hysteresis loop along the magnetic field axis.



FIGURE 1. Temperature dependence of the saturation magnetization and remanence for magnetite.



FIGURE 2. Temperature dependence of the coercivity and exchange bias field for magnetite.

Fig. 3 shows the temperature dependence of the saturation magnetization (M_8) and remanence (M_R) for nanocomposites with different filler contents. Fig. 4 shows the coercivity (H_C) and exchange bias field (H_{eb}) as a function of temperature for nanocomposites. The result had shown that all the magnetic parameters increase when the temperature decreases from 298 to 93 K. The magnetization for nanocomposites increase with Fe₃O₄ nanoparticles content in the TPNR matrix. This is probably due to the effect of inter-particles interaction in magnetic properties. When the plot of coercivity as a function of temperature is observed carefully, we found that the coercivity for nanocomposites with 4 wt% of filler is always higher than the nanocomposites with 12 wt% of filler along the whole range of temperature. This suggest that the lower filler content in matrix TPNR has heightened the anisotropy energy due to dipolar interactions. When the average inter-particle distances are increased, as in the case when they are dispersed in matrix polymer, the anisotropy barrier effectively increases. The exchange bias field for all of the nanocomposites is in the range of 50-60 Oe, which is much higher than Fe_3O_4 nanoparticles, with the exchange bias field always less than 1 Oe. The origin of the strange behavior of nanocomposites might be related to two characteristics of the samples. Firstly, the intra-particle exchange interaction, or the exchange coupling between the AFM and FM components at the interface. Secondly, the inter-particle dipolar interactions between the neighboring particles. By dispersing the nanoparticles in matrix TPNR, the inter-particle dipolar interactions effectively decreasing in strength and becoming dominant over the intra-particle exchange interaction. Hence, the exchange bias field for nanocomposites is much higher than nanoparticles.



FIGURE 3. Temperature dependence of the saturation magnetization and remanence for nanocomposites.



FIGURE 4. Temperature dependence of the coercivity and exchange bias field for nanocomposites.

CONCLUSIONS

Saturation magnetization, remanence, coercivity and exchange bias field of Fe_3O_4 nanoparticles increase with decreasing temperature. Oxide ferrimangetic, Fe_3O_4

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exhibit exchange bias effects due to the ferrimagnetic and antiferromagnetic components at the interface. "Spin glass like" layer at the surface of nanoparticles play the role as an "AFM" in the ferromagnetic particles. It is observed that inter-particle effects such as dipolar interaction are reduced as the particles are separated from each other by the TPNR.

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