

MAGNETIC BEHAVIOR OF MAGNETITE NANOPARTICLES AND ITS NANOCOMPOSITES

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Introduction

Nanostructured magnetic materials have been a subject of great scientific and technological interest in recent years. They may exhibit phenomena such as enhanced coercivity, reduced saturation magnetization and superparamagnetism [1]. These nanostructural materials have been used as filler in the polymeric matrices to fabricate magnetic polymer nanocomposite which have been an active area of recent research, owing to their range of applications in electromagnetic interference shielding (EMI) [2-3], drug delivery, drug targeting and as contrasting agent in magnetic resonance imaging (MRI) [4]. There are two methods for the formation of magnetic polymer nanocomposites, simplest it is incorporating to polymer magnetic particles previously formed, grinding them and mixing them with polymer. The other method is the synthesis in-situ of nanoparticles within a polymeric matrix [5]. In this work, we have chosen thermoplastic natural rubber as polymer matrix and nanosized magnetite (Fe_3O_4) as the fillers. Magnetite filled thermoplastic natural rubber nanocomposites were prepared by melt blending method and the temperature dependence of the magnetic properties of Fe_3O_4 nanoparticles and its nanocomposites were studied at our laboratory.

Experimental

Materials

Fe_3O_4 nanoparticles, with the particle size ranging from 20-30 nm, were obtained from commercial suppliers in powder form (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.

Preparation of nanocomposites

TPNR filled Fe_3O_4 nanocomposites with 0 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. Blending was carried out with mixing speed of 100 r.p.m. at 180 °C for 13 mins. The NR was initially melted in an internal mixer. The LNR, which was previously mixed with Fe_3O_4 nanoparticles was then added into the internal mixer 3 mins after the blending started. NR, LNR and the nanoparticles were allowed to mix for 4 mins before PP was charged into the internal mixer.

Characterization

The resulting nanocomposites were characterized by X-ray diffraction using CuK (1.54 Å) radiation and the magnetic properties were studied by a vibrating sample magnetometer (Model VSM 7404) in term of the effect of temperature on magnetization. The specimens for magnetic measurements were made into disc shape of 5 mm in diameter. The sample was first cooled down to 6 K without applied magnetic field and then the magnetization of the samples were measured from 6 to 298 K in the maximum applied magnetic field of 12 kOe. The applied field was applied parallel to the sample.

Results and Discussion

Fig. 1. X-ray diffraction patterns of pure TPNR, pure nanoparticles and nanocomposites at different filler contents.

X-ray diffraction patterns of pure TPNR, pure Fe_3O_4 nanoparticles and nanocomposites at different filler contents are shown in Fig. 1. For pure Fe_3O_4 nanoparticles, it is found that there are a series of characteristic peaks at $2\theta = 30.34^\circ, 35.62^\circ, 43.18^\circ, 53.66^\circ$ and 57.22° which can be assigned to (2 2 0), (3 1 1), (4 0 0), (4 2 2) and (5 1 1) planes of Fe_3O_4 respectively (JCPDS 01-1111). The d values calculated from the XRD patterns are well indexed to the cubic spinel phase of Fe_3O_4 with the lattice parameter of $a = 8.395$ with no impurity phases detected. The crystallite size, D , calculated from XRD peak broadening using Debye-Scherrer's formula ($D = k / \cos \theta$, $k = 0.9$, θ is the X-ray wavelength, $\Delta 2\theta$ is the FWHM of the (3 1 1) peak and 2θ is its peak position) is 22 nm. The X-ray diffraction patterns of the nanocomposites comprise of two phases which are the crystalline and amorphous phases. It can be seen that the crystallinity increases with the addition of Fe_3O_4 nanoparticles. This is due to the addition of crystalline Fe_3O_4 which migrates

into the amorphous phase of TPNR, reducing the amorphous domains of the TPNR sample [6]. The diffraction patterns also indicate that the structure of Fe_3O_4 in the nanocomposites is maintained.

(a)

(b)

(c)

Fig. 2. Temperature dependence of the saturation magnetization (M_S), retentivity (M_R) and coercivity (H_C) for Fe_3O_4 nanoparticles and nanocomposites.

The typical temperature dependence of the saturation magnetization (M_S), retentivity (M_R) and coercivity (H_C) for Fe_3O_4 nanoparticles and nanocomposites with different filler contents at applied field of 12 kOe are shown in Fig. 2. The saturation magnetization for Fe_3O_4 nanoparticles at room temperature (298 K) is 63.79 emu/g, which is lower than bulk Fe_3O_4 (92 emu/g) [7]. The reduction in saturation magnetization may be attributed to the surface disorder or spin canting at the particles surface [8]. In the temperature range of 28 to 298 K, magnetization for both nanoparticles and nanocomposites increases 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 [9]. At lower temperatures (<28 K), the magnetization decreases with decreasing temperature. As shown in the inset of Fig. 2(a), the magnetization versus temperature plot for nanoparticles exhibits a small cusp in the magnetization. The position of the maxima is an indication of blocking temperature, T_B (~28 K). The magnetic moments of the nanoparticles are blocked below this temperature.

When the plot of coercivity as a function of temperature is observed, we found that the coercivity for nanocomposites with different filler contents are always higher than the pure Fe_3O_4 nanoparticles along the whole range of temperature. The lowered H_C for the pure nanoparticles may be the result of a lowered anisotropy barrier 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 [1]. In Fig. 2(c), it is evident that the coercivity increases as the temperature is decreased. The increment in coercivity with decreasing temperature is the result of an increment in AFM anisotropy energy barriers, K_{AFM} with decreasing temperature, which is due to the exchange coupling between the ferro or ferrimagnetic (FM) and antiferromagnetic (AFM) components at the interface [10].

Conclusion

Magnetic polymer nanocomposites of TPNR and Fe_3O_4 nanoparticles were successfully prepared. The nanoparticles were dispersed into TPNR in varying concentrations. Both the nanoparticles and nanocomposites exhibited a blocking temperature of ~28 K. Below the blocking temperature, a decrease in saturation magnetization have been observed. The increased in coercivity with decreasing temperature is due to the surface effects arise in pure nanoparticles, as the size is reduced.

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