

Sains Malaysiana 41(9)(2012): 1125–1131

## Structural and Magnetic Properties of Type-M Barium Ferrite – Thermoplastic Natural Rubber Nanocomposites

(Sifat Struktur dan Magnet Nanokomposit Ferit Barium Jenis-M – Getah Asli Termoplastik)

NURHIDAYATY MOKHTAR, MUSTAFFA HJ. ABDULLAH\* &amp; SAHRIM HJ. AHMAD

### ABSTRACT

Structural and magnetic properties of type-M barium ferrite ( $BaFe_{12}O_{19}$ ) nanoparticles ( $\sim 20$  nm) embedded in non-magnetic thermoplastic natural rubber (TPNR) matrices were investigated. The TPNR matrices were prepared from high density polyethylene (HDPE) and natural rubber (NR) in the weight ratios of 80:20 and 60:40, respectively, with 10 wt% of NR in the form of liquid natural rubber (LNR) which act as a compatibiliser.  $BaFe_{12}O_{19}$ -filled nanocomposites with 2 – 12 wt%  $BaFe_{12}O_{19}$  ferrite were prepared using a melt-blending technique. Magnetic hysteresis was measured using a vibrating sample magnetometer (VSM) in a maximum field of 10 kOe at room temperature (25°C). The saturation magnetisation ( $M_s$ ), remanence ( $M_r$ ) and coercivity ( $H_c$ ) were derived from the hysteresis loops. The results show that the structural and magnetic properties of nanocomposites depend on both the ferrite content and the composition of the natural rubber or plastic in the nanocomposites. All the nanocomposites exhibit an exchange bias-like phenomenon resulting from the exchange coupling of spins at the interface between the core ferrimagnetic region and the disordered surface region of the nanoparticles.

**Keywords:** Exchange bias; high density polyethylene; hysteresis; magnetic properties; natural rubber

### ABSTRAK

Sifat struktur dan magnet nanozarah ( $\sim 20$  nm) ferit barium jenis-M ( $BaFe_{12}O_{19}$ ) yang dimasukkan ke dalam matriks getah asli termoplastik (TPNR) tidak bermagnet telah dikaji. Matrik TPNR disediakan daripada polietilena ketumpatan tinggi (HDPE) dan getah asli (NR) dalam nisbah berat 80:20 dan 60:40, dengan 10% berat NR dalam keadaan getah asli cecair (LNR) yang bertindak sebagai penserasi. Nanokomposit berpengisi  $BaFe_{12}O_{19}$  sebanyak 2 – 12% berat disediakan menggunakan teknik adunan lebur. Histeresis magnet diukur menggunakan magnetometer sampel bergetar (VSM) dalam medan maksimum 10 kOe pada suhu bilik (25°C). Pemagnetan tepu ( $M_s$ ), remanens ( $M_r$ ) dan koersiviti ( $H_c$ ) diperolehi daripada gelung histeresis. Keputusan menunjukkan bahawa sifat struktur dan magnet nanokomposit bergantung kepada kandungan ferit dan komposisi getah asli atau plastik dalam nanokomposit. Semua nanokomposit menunjukkan fenomena mirip pincang saling tukar yang terhasil daripada gandingan saling tukar pada antaramuka di antara rantau teras ferimagnet dan rantau tak tertib di permukaan nanozarah.

**Kata kunci:** Getah asli; histeresis; pincang saling tukar; polietilena ketumpatan tinggi; sifat magnet

### INTRODUCTION

Barium ferrite type-M,  $BaFe_{12}O_{19}$ , is one of the several hexaferrites with a general formula  $Ba_l M_m^{2+} Fe_{2n}^{3+} O_{1+m+3n}$ , where  $l$ ,  $m$  and  $n$  are integers and  $M^{2+}$  is a divalent transitional metal ion. Type-M hexaferrites of barium and strontium are very important components in permanent magnets, magnetic recording media, microwave and high frequency devices. The attractive properties of these materials are high magnetisation, remanence, coercivity and electrical resistivity. The materials also have great resistance to high temperature, humidity, chemicals and corrosion. The materials have become increasingly useful for various applications when particles of various shapes and sizes are incorporated into magnetic or non-magnetic matrices. By using a non-magnetic polymeric matrix, the properties of the resulting polymer-bonded magnet

(PBM) can be varied for specific applications. The advantages of PBMs over their metallic and ceramic counterparts are their ability to be moulded into complex shapes and sizes, light weight and comparably low cost.

Among the polymeric matrices, thermoplastic natural rubber (TPNR) has been used by some researchers (Abdullah et al. 2007; Hamid et al. 2002; Kong et al. 2010; Puryanti et al. 2007; Yusoff et al. 2002). TPNRs are essentially the blend of natural rubber and various conventional plastics in certain proportions. In the present work, the high density polyethylene (HDPE) was used. Barium ferrite ( $BaFe_{12}O_{19}$ ) nanoparticles are used as filler. The magnetic properties as a function of composition of the ferrite filler for two different TPNRs with different ratios of NR/HDPE were investigated.

## EXPERIMENTAL METHODS

## MATERIALS

BaFe<sub>12</sub>O<sub>19</sub> powder with particle size of about 20 nm (purity 99.99%) was supplied by Nanostructured & Amorphous Materials, Inc., USA. Natural rubber (NR) and high density polyethylene (HDPE) were supplied by Rubber Research Institute of Malaysia (RRIM) and Mobil (M) Sdn. Bhd., respectively. Liquid natural rubber (LNR) was prepared via photosensitised degradation of NR in visible light. A desired amount of NR cut into small pieces was soaked in toluene in a round flask for 24 h. A solution of methylene blue and Rose Bengal in methanol was then added to the swollen NR. The mixture was exposed to a 500 W halogen lamp while being stirred continuously by means of mechanical stirrer for a few days until all the NR was degraded to LNR.

Barium ferrite - filled TPNR nanocomposites with 2 – 12 wt% of BaFe<sub>12</sub>O<sub>19</sub> were prepared by the melt-blending technique using a laboratory mixer (Model Thermo Haake). The weight ratios and NR are 80:20 and 60:40, with 10% NR in the form of LNR as compatibiliser. The NR was initially melted in the mixer for 3 min. The LNR, which had been previously mixed with BaFe<sub>12</sub>O<sub>19</sub> nanoparticles, was then added into the mixer. The mixture was allowed to mix at 100 rpm for 4 min. before HDPE was charged into the mixer. Homogeneous mixing was assumed after 13 min. The blend was removed from the mixer and subsequently pressed at 140°C under 45 Mpa of pressure for about 2 min. using a hot press (Model Carver Laboratory Press) into a thin sheet of 0.1 mm in thickness. The nanocomposites are identified as series H and L for TPNR matrices of 80HDPE/20NR and 60HDPE/40NR, respectively.

## CHARACTERISATIONS

A transmission electron microscope (TEM) model Philips CM12 was used to study the sizes and shapes of the pure BaFe<sub>12</sub>O<sub>19</sub>. The X-ray diffraction (XRD) on the nanocomposites was carried out using a Siemens D5000 Diffractometer with CuK<sub>α1</sub> radiation ( $\lambda = 1.541 \text{ \AA}$ ) in the  $2\theta$  range of 5 – 80° in steps of 0.02° over 3 h. Magnetic hysteresis was obtained using a vibration sample magnetometer (VSM, Lakeshore 7400 Series) in a maximum field of 10 kOe. The external magnetic field was applied parallel to the plane of the sample in the form of a disc of about 3 mm in diameter and 0.1 mm in thickness, so that the demagnetising factor is negligible.

## RESULTS AND DISCUSSION

## STRUCTURAL PROPERTIES

The micrograph shown in Figure 1(a) for the pure BaFe<sub>12</sub>O<sub>19</sub> filler indicates that the particles are hexagonal of size about 20 nm. Figures 1(b) and 1(c) show the SEM micrographs for two samples from L series with 2 wt. % (L2) and 8 wt. % (L8) filler contents, respectively. It

can be concluded that the filler particles are uniformly distributed throughout the TPNR matrix. The filler particles are identified as the bright spots in the micrographs. The results and conclusion from the other samples of L series and H series are similar.

Figure 2 shows the X-ray diffractograms of both TPNRs, pure BaFe<sub>12</sub>O<sub>19</sub> nanoparticles and series H

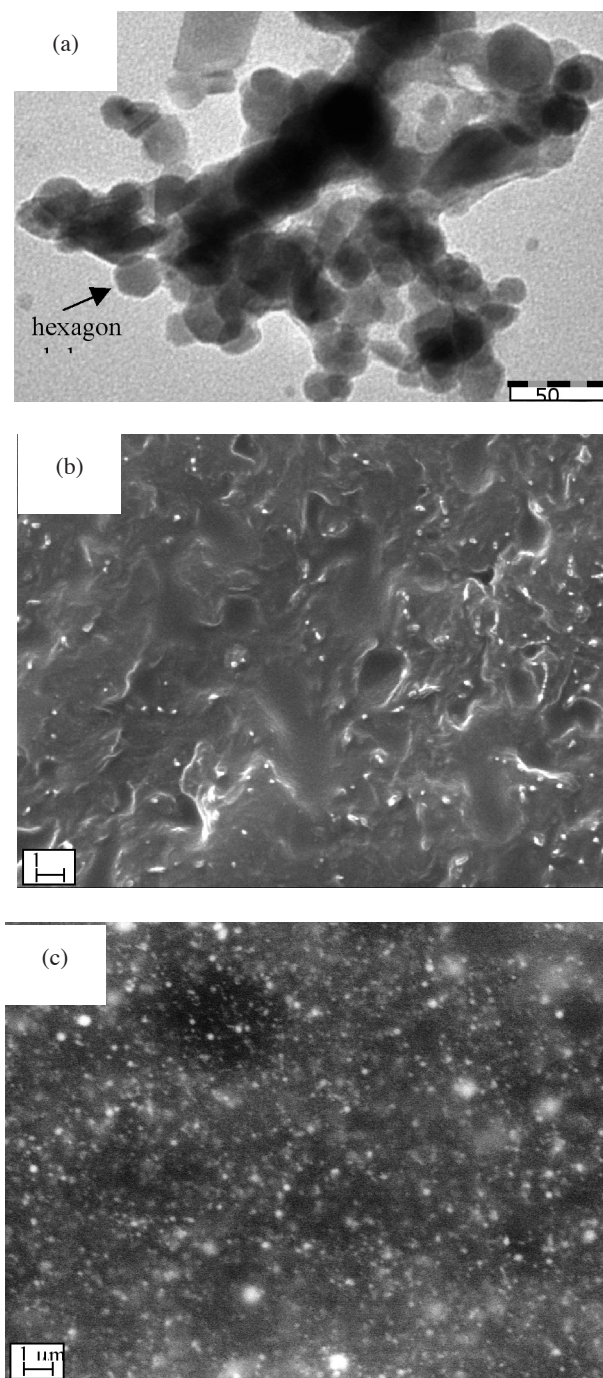


FIGURE 1. (a) TEM micrograph for pure BaFe<sub>12</sub>O<sub>19</sub> BaFe<sub>12</sub>O<sub>19</sub> nanoparticles (magnification 60,000 ×). (b) and (c) are SEM micrographs for L2 and L8, respectively (magnification 5,000 ×)

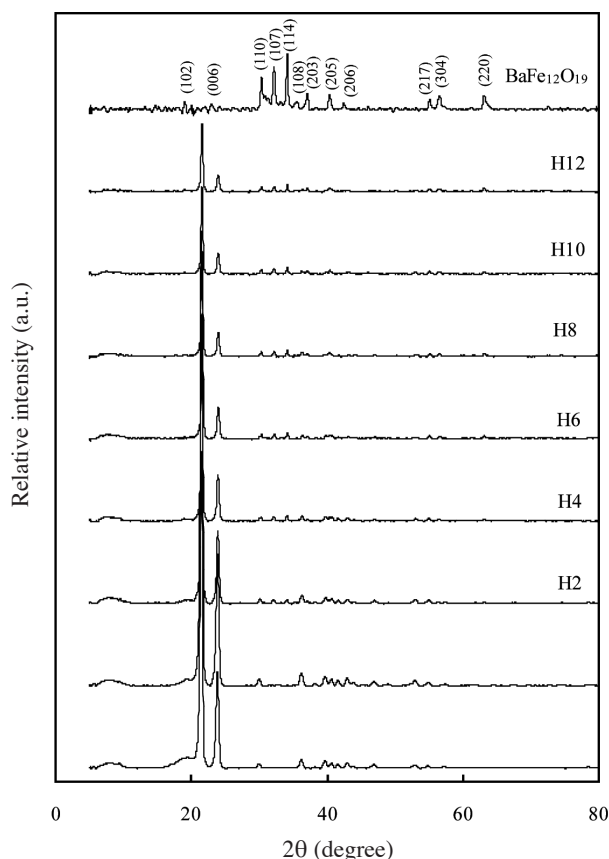


FIGURE 2. X-ray diffractograms for pure materials and nanocomposites (series H). H2, H4, H6, H8, H10 and H12 refer to nanocomposites with 2, 4, 6, 8, 10 and 12 weight % of  $\text{BaFe}_{12}\text{O}_{19}$  filler

nanocomposites with different filler contents.  $\text{BaFe}_{12}\text{O}_{19}$  was characterised by peaks at  $2\theta$  (degree) = 19.04, 23.00, 30.35, 32.18, 34.15, 35.54, 37.12, 40.36, 42.50, 55.15, 56.61 and 63.11, which correspond to (1 0 2), (0 0 6), (1 1 0), (1 0 7), (1 1 4), (1 0 8), (2 0 3), (2 0 5), (2 0 6), (2 1 7), (3 0 4) and (2 2 0) atomic planes, respectively (JCPDS 00-043-0002). The lattice parameters calculated from the XRD patterns for hexagonal structure are  $a = 5.893 \text{ \AA}$  and  $c = 23.194 \text{ \AA}$ .

The diffractograms indicate that the present TPNRs (80HDPE/20NR, labeled as H series and 60HDPE/40NR, labeled as L series) are semicrystalline, as there are sharp peaks at  $2\theta = 21.6^\circ$  and  $24.0^\circ$  arising from crystalline region and a weak, broad peak centred about  $19.5^\circ$  due to the amorphous region. The intensity of these peaks decreases with increasing barium ferrite content. Similar peaks have been observed in TPNRs matrices of PP/NR (Hamid et al. 2002), HDPE/NR (Puryanti et al. 2006) and PP/NR (Kong et al. 2010). X-ray study on TPNR (PP/NR) by Hamid et al. (2000) confirmed that the peaks in the semicrystalline matrix of TPNRs are due to the plastic component or PP in the matrix, as the result showed that the peaks were diminishing with the decrease in PP in the TPNR matrix. It is also shown in this study that the intensity of the semicrystalline peaks in TPNR with higher

HDPE are higher compared with those from TPNR with lower HDPE, indicating that the semicrystalline property of TPNR is due to the HDPE plastic. The patterns from the nanocomposites indicate the presence of two phases, which are the crystalline and semicrystalline phases due to  $\text{BaFe}_{12}\text{O}_{19}$  and TPNR, respectively.

#### MAGNETIC PROPERTIES

**Magnetic hysteresis** Magnetic hysteresis for pure  $\text{BaFe}_{12}\text{O}_{19}$  is shown in Figure 3(a), while those for the nanocomposites (H series) are shown in Figure 3(b). The samples are not fully saturated at 10 kOe, but the saturation seems achievable for low-filler samples. It is expected that the saturation magnetization will be slightly higher at higher magnetic field. The maximum magnetisation in 10 kOe ( $M_m$ ) from the present  $\text{BaFe}_{12}\text{O}_{19}$  sample is 31.22 emu/g, while the remanence  $M_R = 17.48$  emu/g and coercivity  $H_c = 3821$  Oe. The present  $\text{BaFe}_{12}\text{O}_{19}$  nanoparticles (about 20 nm) are single domain non-superparamagnetic as the critical diameters for single domain and superparamagnetism for  $\text{BaFe}_{12}\text{O}_{19}$  are 460 nm (Rezlescu et al. 1999) and 10 nm (Rane et al. 1999), respectively. For comparison the saturation magnetisation of the bulk type-M barium ferrite has been reported as 70 emu/g (Kojima 1982).

**Magnetisation** Figures 4 and 5 show the maximum magnetisation ( $M_m$ ) and remanence ( $M_R$ ) as a function of filler content for both TPNR compositions of 80HDPE/20NR (H) and 60HDPE/40NR (L). The variations of  $M_m$  and also  $M_R$  for both series are similar, but the values for series H are lower than those for series L. As expected, both quantities increase with increasing ferrite content. It is expected that the total magnetisation of the nanocomposites is only due to the ferrite filler, as TPNR is non-magnetic. Hence, it can be assumed that the magnetisation of the composite sample,  $M_{mc} = w M$ , where  $M$  is the magnetisation of the ferrite and  $w$  is the weight percentage of the ferrite in the nanocomposites. It is expected that the graphs for the two composites to overlap. However, the results in Figure 4 show that there is a considerable difference in the values between the two series and are different from the calculated values.

Magnetic nanoparticles are generally divided into a core region of ordered spin arrangement and a surface or shell region with structural and spin disorder (Kodama et al. 1996, 1997). Disordered spins are the main reason for reduced magnetisation in nanoparticle systems. Surface spin disorder in ferrite nanoparticles largely arises from the breakage of superexchange bonds due to the missing oxygen ions that mediated the superexchange interaction between cations (Misra et al. 2004). The region is sharply increased with the decrease in particles size, so that more spins disorder occurs within the same volume of the material, resulting in the reduction in magnetisation. The present results show that the proportion of disordered spin changes when the ferrite nanoparticles are embedded in



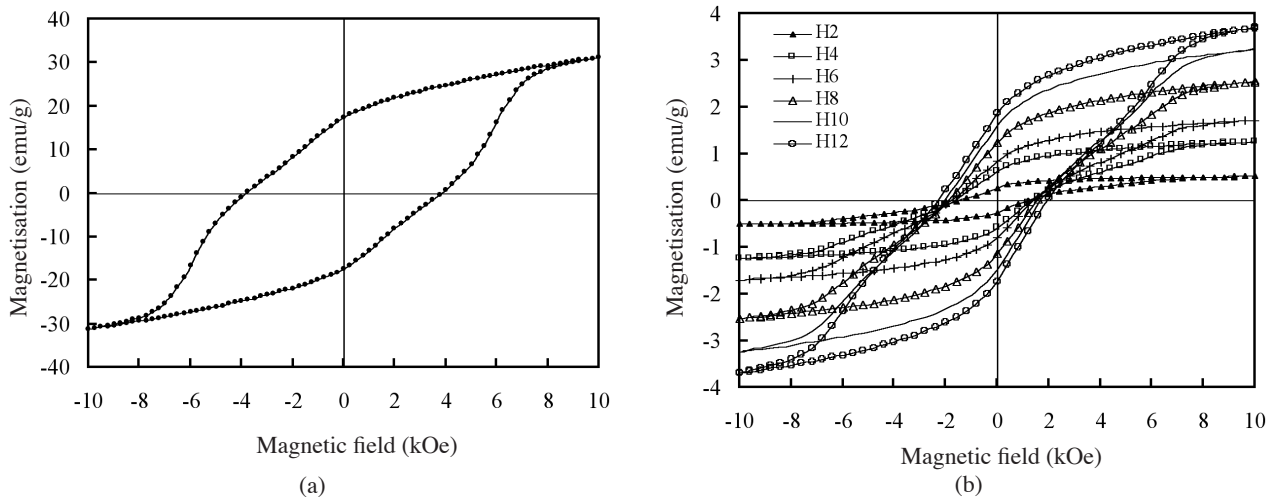


FIGURE 3. Magnetic hysteresis for (a)  $\text{BaFe}_{12}\text{O}_{19}$  nanoparticles, and (b)  $\text{BaFe}_{12}\text{O}_{19}$  – TPNR (Series H) nanocomposites

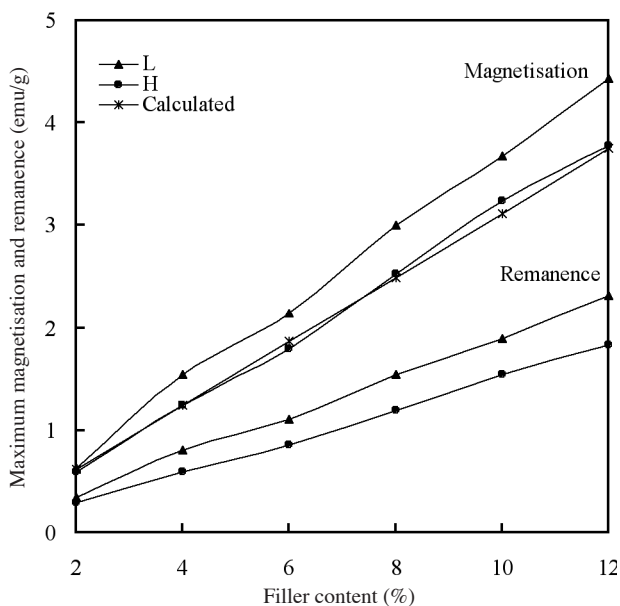


FIGURE 4. Maximum magnetisation ( $M_m$ ) and remanence ( $M_R$ ) of the nanocomposites for different filler contents

TPNR of different compositions or plastic to natural rubber ratios. It was found that the magnetisation of L series, with low content of HDPE plastic, is higher than that for H series with higher plastic (HDPE) content. It seems that the NR component in the TPNR tends to reduce the disordered spin or shell region in the nanoparticles. It is believed that the higher magnetisation of the L series nanocomposites is due to the natural rubber providing the mediating ions for superexchange interaction. As a result the spin disorder decreased and the effective magnetic moment is increased when the composition of natural rubber in the nanocomposites is increased. In other words, the proportion of core spins is increased, so that  $M_m$  is increased relative to the calculated values.

**Remanence** Figure 5 shows the variation of remanence ( $M_R$ ) and remanence ratio ( $R = M_R/M_m$ ) for both series of nanocomposites. The values of  $R$  indicate that about 50% of the magnetisation of the nanocomposites are preserved when the magnetic field is reduced from 10 kOe to zero. This property resulted in the variation of remanence very similar to the maximum magnetisation. The remanence ratios for both series are minimum at about 8% weight of filler.

**Coercivity** The variations of the average values of coercivity as a function of filler content for both series are shown in Figure 6. The results show that  $H_c$  is linearly increased with the increase in filler content. It is interpreted that a stronger force is needed to bring the larger number of the core spins back to random state, thus the higher values of  $H_c$  for samples with higher filler content.  $H_c$  values for series L are higher than those for series H, but the values are less sensitive to the incremental change of the ferrite filler. The resistance to spin rotation on reducing the external field is higher for nanocomposites with higher NR in the TPNR. The larger effective magnetic moment in the L series allows a stronger interparticle interaction which is believed to contribute positively to the effective magnetic anisotropy constant, thus producing larger coercivity compared with the H series.

**Exchange Bias** It is interesting to consider the coercivity on both sides of the axis as there is a shift in the values of  $H_c$  for all the nanocomposites, as shown in Figure 7. The shift in  $H_c$  is defined as  $H_s = (H_{c2} - H_{c1})/2$ , where  $H_{c1}$  and  $H_{c2}$  are the absolute values of coercivity on the positive and negative axes respectively (Hajra et al. 2009). The shift for H series nanocomposites are in the range of 140 – 170 Oe, while those for L series nanocomposites are in the range of 90 – 110 Oe. The shift in hysteresis loop has been discussed as the exchange bias phenomenon in many systems that are composed of ferromagnetic

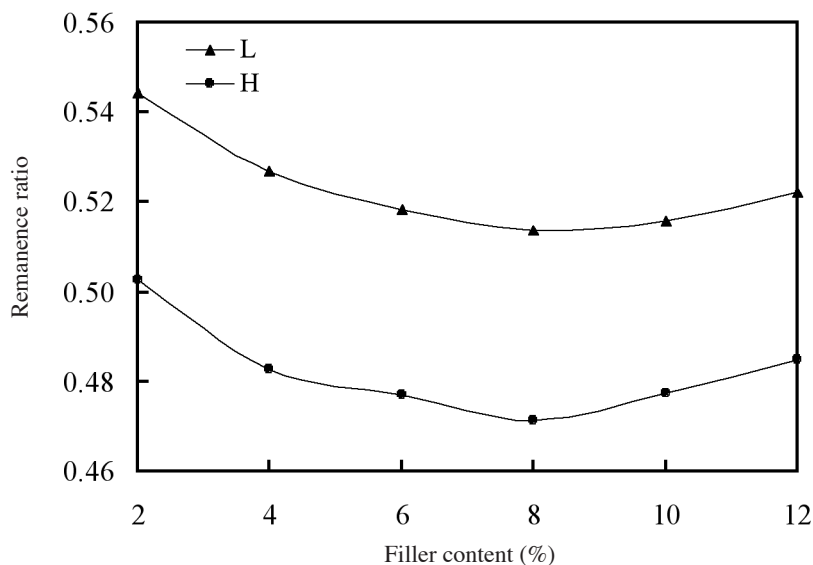


FIGURE 5. Remanence ratio (R) of the nanocomposites for different filler contents

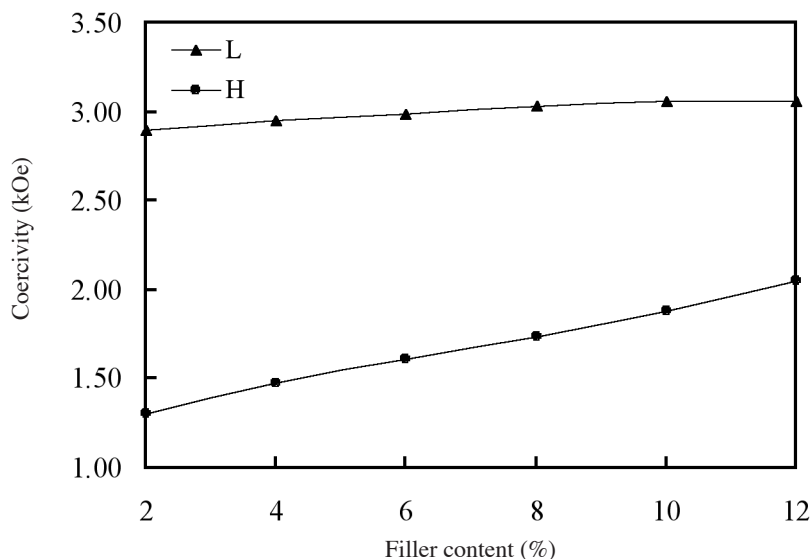


FIGURE 6. Coercivity ( $H_c$ ) of the nanocomposites for different filler contents

and antiferromagnetic multilayers (Nogues & Schuller 2005). In the present ferrite nanocomposites, the model by Berkowitz et al. (1975, 1980) and Kodama et al. (1996) where nanoparticles consist of a ferrimagnetically aligned core and a disordered spin glass-like layer at the surface is plausible. The present result shows no exchange bias in pure  $BaFe_{12}O_{19}$  nanoparticles. The TPNR matrix is essential in promoting the exchange bias in the present nanocomposites. It could be due to the effect of TPNR is the pinning of the surface spins in a manner described by Berkowitz et al. (1975) on the behaviour of nickel ferrite nanoparticles coated with organic molecules.

The exchange bias-like in the ferrite nanoparticles then arises from the exchange coupling between spins in the core and disordered spins in the shell regions of the

nanoparticles. The H series nanocomposites has a larger surface spin disorder, thus a larger surface anisotropy. This larger surface anisotropy field is responsible for stronger pinning and subsequently larger loop shift in the H series nanocomposites.

#### CONCLUSION

The magnetic properties of  $BaFe_{12}O_{19}$  - TPNR (HDPE/NR) depend both on the filler content and compositions of plastic and natural rubber in the TPNR matrix. The increase in the NR in the TPNR matrix is not only found to increase the magnetisation, remanence and coercivity, but also to increase the exchange bias. The TPNR matrix promotes the exchange bias in the  $BaFe_{12}O_{19}$  - TPNR nanocomposites

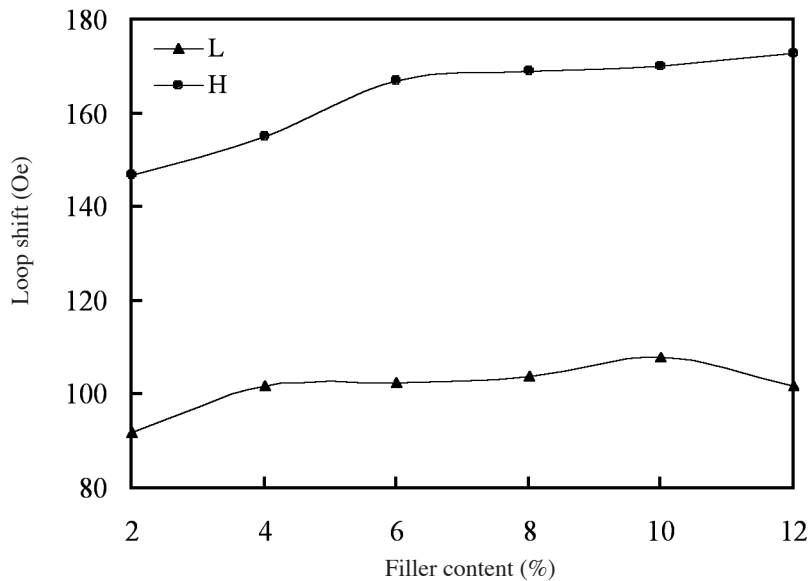


FIGURE 7. The shift in coercivity of nanocomposite for different filler contents

#### ACKNOWLEDGEMENT

The authors would like to thank Universiti Kebangsaan Malaysia and Universiti Putra Malaysia for research facilities and financial assistance for this project.

#### REFERENCES

- Abdullah, M.H., Ahmad, M., Ibrahim, N.B. & Yusoff, A.N. 2008. Microwave magnetic, dielectric and absorption properties of some cerium yttrium iron garnets. *Sains Malaysiana* 37(2): 205-210.
- Berkowitz, A.E., Lahut, J.A., Jacos, I.S., Levinson, C.M. & Forester, D.W. 1975. Spin Pinning at Ferrite-Organic Interfaces. *Physical Review Letters* 34: 594-598.
- Berkowitz, A.E., Lahut, J.A. & Van Buren, C.E. 1980. Properties of magnetic fluid particles. *IEEE Transactions on Magnetics*, MAG-16: 184-190.
- Hajra, P., Basu, S., Brahma, P. & Chkravorty, D. 2009. Exchange bias in ferromagnetic-antiferromagnetic nanocomposite produced by mechanical attrition. *Journal of Magnetism and Magnetic Materials*. 321(14): 2269-2275.
- Hamid, S.A.A., Abdullah, M.H., Ahmad, S.H., Jusoh, Mansor, A.A. & Yusoff, A.N. 2002. Effects of natural rubber on microwave absorption characteristics of some Li-Ni-Zn ferrite – thermoplastic natural rubber composites. *Japanese Journal of Applied Physics*, 41: 5815-5820.
- Hamid, S.A.A., Abdullah, M.H., Ahmad, S.H., Jusoh, Mansor, A.A. & Yusoff, A.N. 2002. Structural and morphological properties of Li-Ni-Zn ferrite – TPNR composites. *Journal of Solid State Science and Technology Letters* 9(1): 68-73.
- Kodama, R.H., Berkowitz, A.E., McNiff, E.J. & Foner, S. 1996. Surface Spin Disorder in NiFe<sub>2</sub>O<sub>4</sub> Nanoparticles. *Physical Review Letters* 77: 394-397.
- Kojima, H. 1982. Fundamental properties of hexagonal ferrites with magnetoplumbite structure. In *Ferromagnetic Materials*, edited by E.P. Wohlfarth. New York: North-Holland Publishing Company.
- Kong, I., Ahmad, S.H., Abdullah, M.H., Hue, D., Yusoff, A.N. & Puryanti, D. 2010. Magnetic and microwave absorbing properties of magnetite – thermoplastic natural rubber nanocomposites. *Journal of Magnetism and Magnetic Materials* 322: 3401- 3409.
- Misra, R.D.K., Gubbala, S., Kale, A. & Egelhoff, Jr, W.F. 2004. A comparison of the magnetic characteristics of nanocrystalline nickel, zinc, and manganese ferrites synthesized by reverse micelle technique. *Materials Science and Engineering B* 111(2-3): 164-174.
- Nogues, J., Sort, J., Langlais, V., Skumryev, V., Surinach, S., Munoz, J.S. & Baro, M.D. 2005. Exchange bias in nanostructure. *Physics Reports* 422(3): 65-117.
- Puryanti, D., Ahmad, S.H., Abdullah, M.H. & Yusoff, A.N. 2007. Effect of nickel-cobalt-zinc ferrite filler on magnetic and thermal properties of thermoplastic natural rubber composites. *International Journal of Polymeric Materials* 56: 1-12.
- Puryanti, D., Ahmad, S.H., & Abdullah, M.H. 2006. Effect of Nickel-Cobalt-Zinc Filler on Electrical and Mechanical Properties of Thermoplastic Natural Rubber Composites *Polymer – Plastics Technology and Engineering* 45: 561-567.
- Rane, M.V., Bahadur, D., Nigam, A.K. & Srivastava, C.M. 1999. Mossbauer and FT-IR studies on non-stoichiometric barium hexaferrites. *Journal of Magnetism and Magnetic Materials* 192(2): 288-296.
- Rezlescue, L., Rezlescue, E., Popa, P.D. & Rezlescue, N. 1999. Fine barium hexaferrite powder prepared by the crystallization of glass. *Journal of Magnetism and Magnetic Materials* 193(1-3): 288-290.
- Yusoff, A.N., Abdullah, M.H., Ahmad, S.H., Jusoh, S.F., Mansor, A.A. & Hamid, S.A.A. 2002. Electromagnetic and absorption properties of some microwave absorbers. *Journal of Applied Physics* 92: 876-882.

Nurhidayat Mokhtar  
Physics Department  
Faculty of Science  
Universiti Putra Malaysia

43400 UPM Serdang  
Selangor D.E.  
Malaysia

Mustaffa Hj. Abdullah\* & Sahrim Hj. Ahmad  
School of Applied Physics  
Faculty of Science and Technology  
Universiti Kebangsaan Malaysia  
43600 UKM Bangi  
Selangor D.E.  
Malaysia

\*Corresponding author; email: mha@ukm.my

Received: 29 June 2011

Accepted: 29 February 2012