Magnetic and mechanical characterisation of natural rubber coprecipitated barium ferrite composites at high loading

M. H. Makled[1] and T. Matsui*[2]

The influence of coprecipitated barium ferrite (BaF) on the magnetic and mechanical properties of natural rubber–ferrite composites (RFCs) has been studied. Unusual characteristics of the BaF particles were revealed by a scanning electron microscope. The results show that the saturation magnetisation increases with increasing the ferrite content even for the considerably high BaF loading samples, whereas the coercivity is almost unchanged. The present RFCs recorded relatively low density 1·95 g cm^{-3} with high stored energy 1·26 MGOe at the maximum BaF loading of 220 phr. Both of the tensile strength and the elongation at break decrease with increasing BaF content. Evaluation of the swelling ratio was carried out to have an insight into the change in the mechanical properties of the RFCs at high BaF loading.

Keywords: Characterisation, Polymer–bonded magnets, Mechanical properties, Percolation

Introduction

Polymers are inherently non-magnetic. The impregnation of magnetic filler in polymer matrix imparts magnetic natures, and considerably modifies the physical properties of the matrix as well. The advantages of polymer bonded magnets (PBMs) over their metallic and ceramic counterparts include low weight, resistance to corrosion, ease of machining and forming and capability for high production rates.[1,2]

The hexagonal ferrites based on $BaFe_{12}O_{19}$ are regarded as an efficient replacement for the metallic magnets using for recording media, microwave devices, etc., due to their high stability in air, non-metallic electrical properties, high volume density, corrosion resistance and low price.[3,4] Hence, the several researches on the composites composed of polymer and such ferrite prepared by ceramic powder method, were performed. However, their magnetic output is always unfavourably low. One of the reasons is the small loading of the ferrite, $\sim$120 phr (part per hundred part of rubber), which should be much less than the expected optimum loading for these kinds of the composites.[5–9] In addition to this, the magnetic ferrite powders prepared by conventional ceramic process are usually known to have much less coercivity and relatively large particle size than those for the ferrite powders made by coprecipitation technique.[10,11] Accordingly, it is worthwhile considering that the coprecipitated hexagonal ferrite–polymer may possibly become a favourable filler for the PBMs, in spite that very little attention for thus material has been paid so far.[12–14]

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An appropriate selection of a polymer matrix as well as a magnetic filler is indispensable for obtaining the composites with required properties for different applications. Natural rubber (NR) has several excellent properties, such as high strength, outstanding resilience and high elongation at break.[15,16] As previously discussed, by using the coprecipitated ferrite, it is not only expected to overcome the undesirable magnetic properties for natural rubber–ferrite composites (RFCs), but also to improve the mechanical properties. The authors have ever previously investigated the magnetic and dynamic mechanical properties of the coprecipitated ferrite–natural rubber composites up to maximum loading of 120 phr, and have revealed that the RFC samples typically showed low density 2·2 g cm^{-3}, high stored energy 1·18 MGOe for the 120 phr samples.[12] In the present studies, the authors will intend to characterise some physical properties of the mentioned composites at high ferrite loading, aiming to tailoring these composites for optimal application for permanent magnets.

Experimental

Materials and preparation of the composites

Hexagonal barium ferrite $BaFe_{12}O_{19}$ (BaF) phase was prepared by the coprecipitated method according to Makled *et al.*[17] Powder having a coercive force 5 kOe, saturation magnetisation 65·5 emu g^{-1}, and 45–200 μm particle size was selected to mix with smoked rubber sheet. The recipe and mixing procedures were reported in the previous paper.[12]

Magnetic measurements

The magnetic properties of the barium ferrite and the rubber ferrite composites were characterised at room temperature under the maximum magnetic field of

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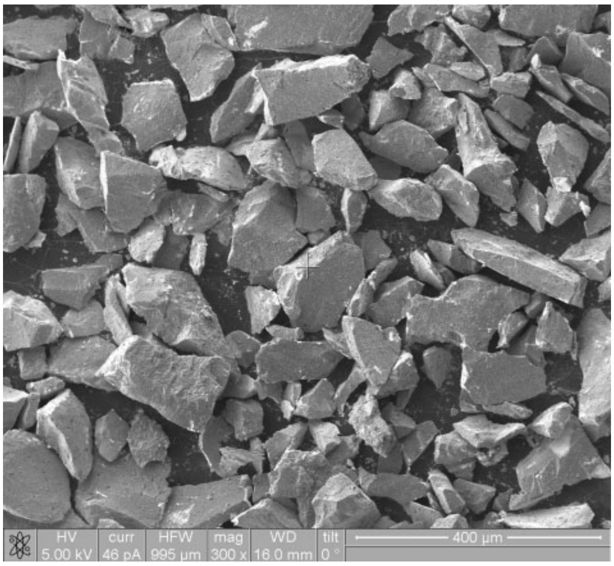
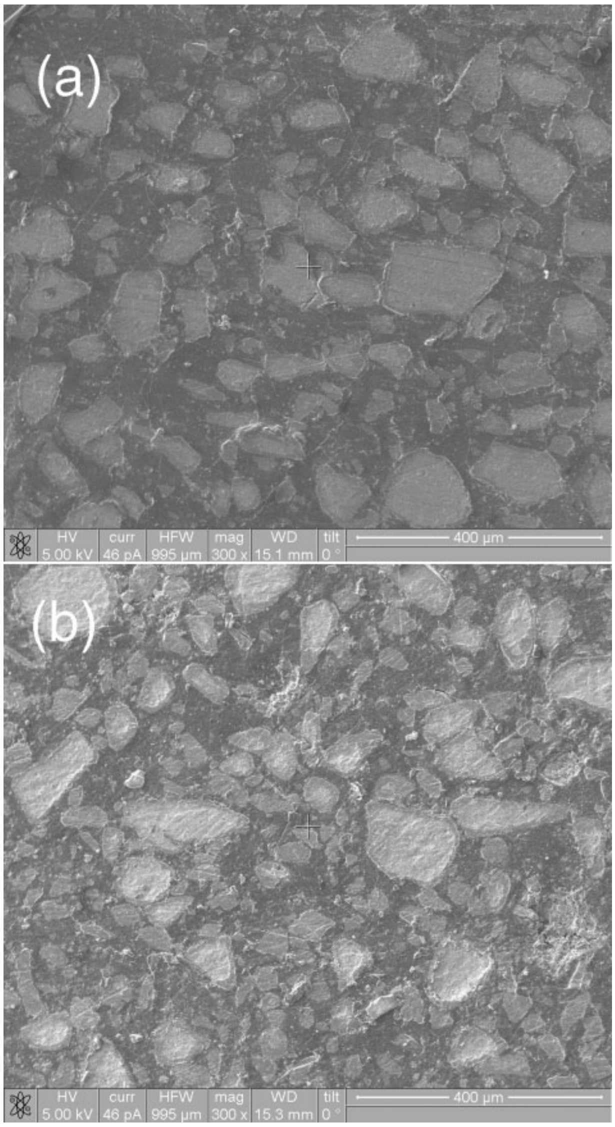


1 Image (SEM) of microstructure of ferrite powder



a 180 phr; *b* 200 phr
2 Images (SEM) of RFC samples

25 kOe by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design: MPMS-XL).

Mechanical properties characterisation

The specimens for dynamic measurements were prepared by moulding the RFCs into the thin sheets with 2 mm thickness at 150°C under 140 kg cm^{-2} hydraulic pressure. The vulcanisation was carried out up to the respective cure times of the samples. The tensile stress was measured according to ASTM D-412, using Shimadzu Tensile System (AG-1000D). ED-120T Electronic Densmeter was used to determine the density of RFCs.

Morphology

Scanning electron microscopy (SEM) observations were performed for the RFCs. The SEM samples were prepared by fracturing the samples and polishing the surfaces under liquid nitrogen, followed by carbon coating.

Swelling test

Swelling test was performed on a test piece weighing about 0·3 g cut from the compression moulded RFC samples. The samples were immersed in pure toluene at room temperature for three days to allow the swelling to reach diffusion equilibrium. Then, the test pieces were taken out and the adhered liquid was rapidly removed by blotting with filter paper. The swelling ratio is defined as

$$R=(W_t-W_0)/W_0$$

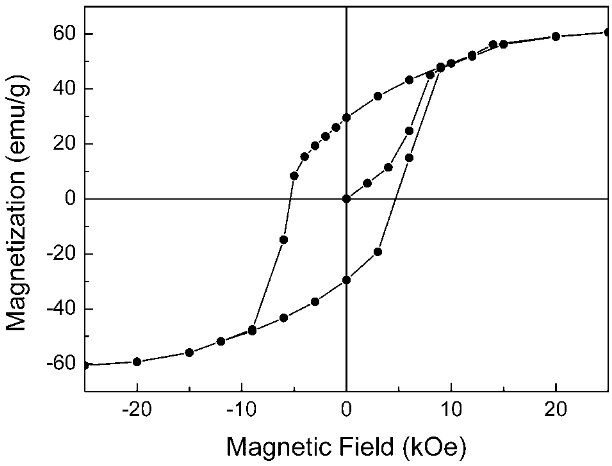
where, W_0 is the weight of test piece before swelling and W_t is the weight of the Swollen test piece after time t of immersion.

Results and discussion

Since the microstructure of the BaF powders as well as the RFCs has already been discussed in details,[18] the authors will describe them briefly here. Figure 1 shows the microstructure of the ferrite powder. It is obvious that the particles are disaggregated and have sharp edges and rather irregular shapes. One of the unusual characteristics of the coprecipitated hexagonal BaF particles is porosity with rough surfaces, which may enhance a good adhesion between the particles and the rubber matrix.

The distribution state of the ferrite particles in the rubber matrixes is shown in Fig. 2*a* and *b* for the 180 and 200 phr samples. The variation of particle size, the broad particle distribution and the homogeneous dispersion can be observed in both figures. It should be noticed in Fig. 2*a* that the initial formation of a cohesive network for the ferrite particles in the rubber matrix, leading to percolation around 180 phr, which is very high in comparison with any different types of fillers.[19–25] The tendency is rather clearly seen in the 200 phr samples as shown in Fig. 2*b*. The retarding of the percolation to very high loading level is unexpected behaviours. The percolation state can be attributed to the nature of coprecipitated ferrite particles and the degree of mixing, which are critical factors in controlling the physical properties of a polymer bonded magnet.[26]

Figure 3 shows the hysteresis loop of the BaF powders. Since the general magnetic single domain size for hexagonal barium ferrite is considered to be around 1 µm, the present BaF particles are expected to have

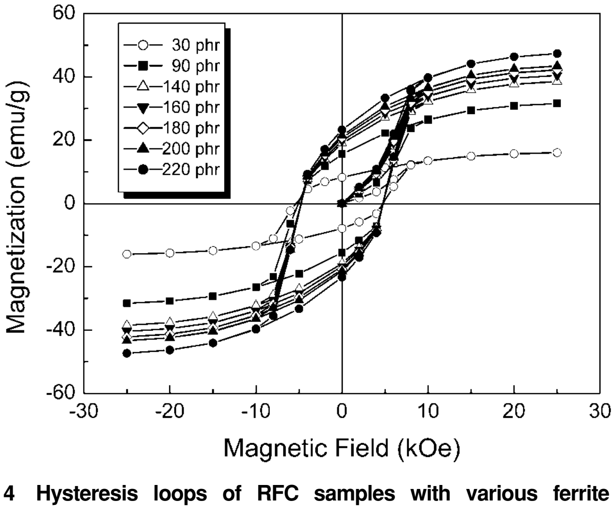


3 Hysteresis loop of coprecipitated ferrite powder

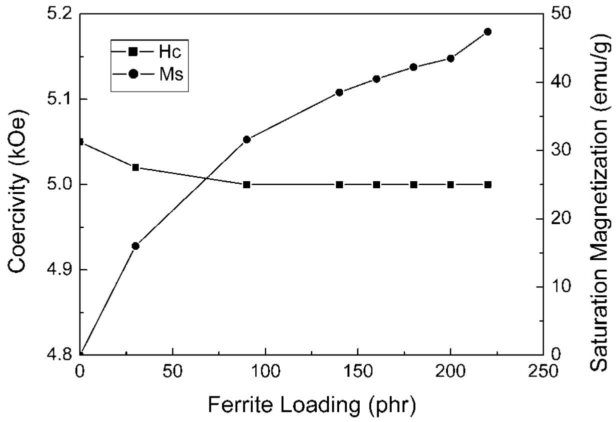
multidomain structure.[10,11] However, the coercivity of the samples exhibited considerably high values of about 5 kOe with the saturation magnetisation of 65·5 emu g^{-1}. They may be ascribed to the present powder preparation method, that is, coprecipitation technique. Since no stress was applied to the particles, the brittleness and porosity should be the main feature of the present particles, which can lead to the high coercivity of the present samples.[27,28]

The variation of the magnetic properties of the RFCs as a function of ferrite loading is shown in Fig. 4. It can be observed that the magnetisation increase with increasing ferrite content. From these curves, the values of the saturation magnetisation M_s and the coercivity H_c for the samples with different BaF loading were determined and plotted in Fig. 5 as a functions of the BaF loading. The figure indicates that the M_s exponentially increases with increasing ferrite content, whereas the change in the coercivity Hc is quite moderate.

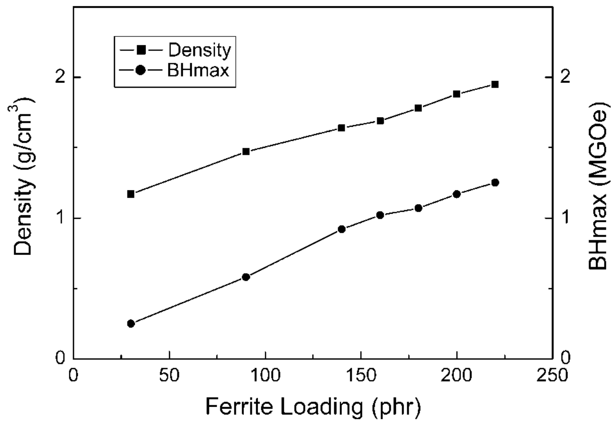
The dependence of the composite density and the maximum energy product $(BH)_{max}$ on the ferrite content is illustrated in Fig 6. Both the $(BH)_{max}$ and the density of the RFCs increase linearly with increasing ferrite content for all the BaF loading samples. The maximum stored energy 1·26 MGOe was obtained for the maximum ferrite loading samples of 220 phr having the relatively low density 1·95 g cm^{-3}. The effect of BaF



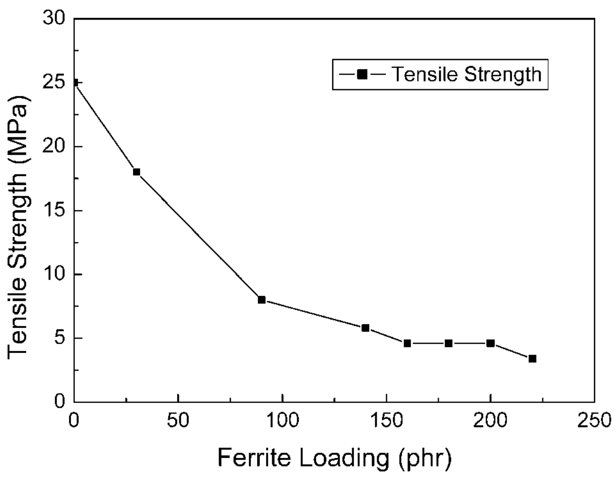
4 Hysteresis loops of RFC samples with various ferrite loadings



5 Variation of H_c and M_s as a function of BaF loading

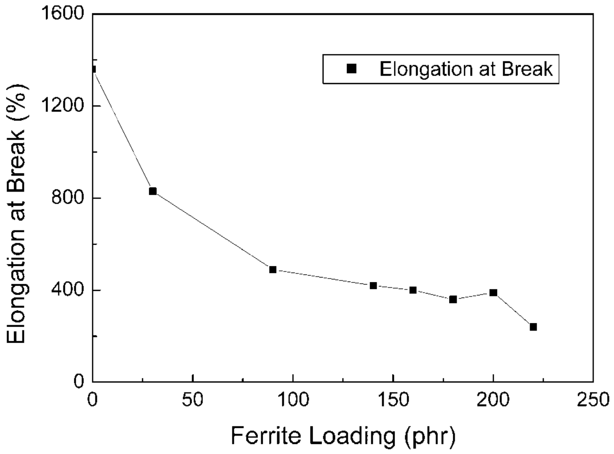


6 Variation of $(BH)_{max}$ and composite density as a function of BaF loading

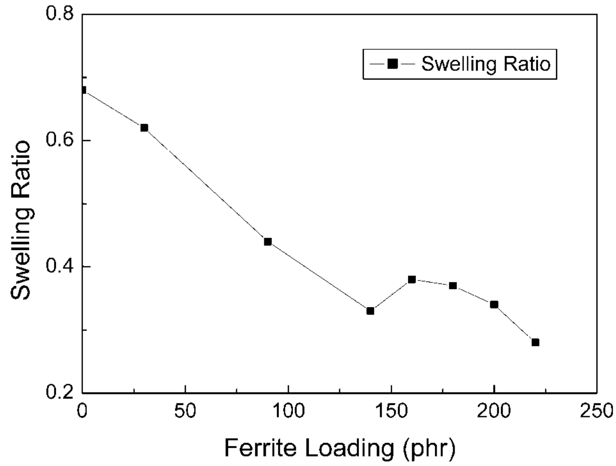


7 Variation of tensile strength of RFCs as a function of BaF loading

addition on the tensile strength for the RFCs is presented in Fig. 7. In the regions of the low ferrite loading, the tensile strength decreases dramatically with increasing BaF content. This is because active fillers usually increase the tensile strength of the composites, whereas inactive fillers reduce it with increasing filler loading.[16,29] Since the BaF filler used in the present studies are considered to be an inactive filler and to have low surface area due to the large particle size, the reduction in the tensile strength can be ascribed to the crystallisation of the NR matrix at initial loading of



8 Variation of elongation at break for RFCs as a function of BaF loading



9 Variation of swelling ratio for RFCs with BaF loading

the filler. Near to the percolation and around 140 phr, the decrease in tensile strength with increasing ferrite loading slows down. This behaviour is compatible to the sudden increase in the cure time, and can be assumed to the change in the vulcanisation mechanism of the present RFCs.[18]

The variation of the elongation at break with the filler loading for the RFCs is shown in Fig. 8. The dependence of the elongation at break on the ferrite content for the RFCs is found to be a similar trend as the tensile strength. For the low ferrite loading samples, the addtion of filler to the polymer matrix reduces chain mobility, giving rise to a rapidly decrease in the elongation at break.

The degree of the adhesion between the filler surfaces and the rubber can be assessed from the swelling behaviour of the samples in a solvent. Therefore, the swelling ratio of the RFCs, which is mainly due to the crosslink density of the composites, influences the mechanical interfacial properties. In other words, the mechanical interfacial properties of the final product are dependent on the swelling ratio.[30]

In order to understand the sudden change in the mechanical behaviour of the present RFCs from around 140 to 200 phr BaF loading, the authors attempted to estimate the swelling ratio. Figure 9 shows the variation of the swelling ratio with increasing BaF loading. It is seen that the swelling ratio decreases with increasing ferrite loading until 140 phr. After 140 phr, the swelling ratio increases slightly with decreasing crosslink density of the RFCs. This decrease in the rubber crosslink can be considered as an inhibitor against the negative effect of the BaF loading on the mechanical properties, leading to an unusual change in the tensile strength and the elongation at break between 140 and 200 phr ferrite loading. The second sharp decrease in both the tensile strength and the elongation at break was noticed after 200 phr (Figs. 8 and 9). The formation of continuous filler network and/or the occurrence of particle agglomeration may be responsible for the appearance of particle–particle contacts instead of polymer–particle contacts, caricaturised by a total lack of adhesion. In this case, a considerable decrease in composite tensile strength at break is observed.[31] This result indicates that even the percolation of the BaF has already occurred at around 180 phr, which means the further addition of the BaF should not affect the mechanical properties of the RFCs. Consequently, 200 phr can be considered as the optimum concentration of the coprecipitated of $BaFe_{12}O_{19}$ in the rubber matrix.

Conclusions

By selecting the disaggregated, high coercivity and low surface energy powder, the mechanical and magnetic properties of the RFCs can be fulfilled in suitable level up to very high level of the ferrite loading. On the other hand, the saturation magnetisation increases with increasing ferrite loading even at high loading. The reduction in the tensile strength is ascribed to the crystallisation of the NR matrix at initial loading of magnetic filler. Consequently, the optimum concentration of BaF in the NR matrix was determined to be 200 phr. The decrease in the rubber crosslink at a certain BaF loading can be considered as an inhibitor against the negative effect of the BaF loading on the mechanical properties.

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