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Effect of Fe Magnetic Nanoparticles in Rubber Matrix

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A new kind of magnetic rubber, Fe dispersed ethylene propylene monomer (EPM), was prepared by a conventional technique using a two roll mill. The magnetic fillers of Fe-nanoparicles were coated by low density polyethylene (LDPE). The purpose of surface treatment of nanoparticles by LDPE is to enhance wettability and lubricancy of the fillers in a polymer matrix. The mechanical strength and microstructure of the magnetic rubber were characterized by tensile strength test and scanning electron microscopy (SEM). Results revealed that the Fe nanoparticles were relatively well dispersed in an EPM matrix. It was found that the nano- Fe dispersed magnetic rubber showed higher coercivity and tensile strength than those of micron- Fe dispersed one.

Keywords : magnetic rubber, ethylene propylene monomer (EPM), nanocomposite

1. Introduction

Recently, polymers filled with magnetic nanoparticles were studied for their applications on adapted tuned vibration absorbers, stiffness tunable mounts and suspensions, and variable impedance surfaces [1-3]. Further improvement of the mechanical and magnetic properties of magnetic rubbers is expected to enable better performance of damping and electromagnetic interference shielding materials. The performance of magnetic rubber device is dependent on mechanical and magnetic properties of composite rubber materials. It was reported that the mechanical properties of magnetic filler dispersed rubber were significantly decreased, though the magnetic properties were enhanced due to large amount of doping concentration of magnetic fillers [4-6]. The magnetic fillers with large particle size have a small surface energy and are unable to form stable adhesive bond with rubber matrix [6]. The properties of an inorganic filler dispersed polymer could be greatly enhanced, when the fillers have nanometer scales [7-9]. However, the preparation of polymers filled with inorganic nanoparticles is very difficult because of hard dispersion of the nanoparticles in the polymer matrix. The nanoparticles are easily agglomerated and separated as immiscible phases in a polymer matrix [5]. This might be the one of the major difficulties for preparation of the polymer nanocomposites, leading them to the unwanted thermal and mechanical properties [9, 10]. To enhance the proper property, the nano-particles must be uniformly dispersed in the polymer matrix.

In this study, Fe nanoparticles were synthesized by pulse wire evaporation (PWE) method [11]. Fabricated Fe fillers have been dispersed in ethylene propylene monomer (EPM) by a conventional technique using a two roll mill [12]. For enhanced dispersion and adhesion strength of nano- and micro- Fe particles in EPM matrix in this study, the surface treatment of the Fe particles was carried out by a stirring low density polyethylene (LDPE) in the cyclohexane [12, 13]. The mechanical and magnetic properties of the Fe nanoparticle reinforced rubber were investigated to reveal adhesion status between particles and matrix, and inter-particle spacing as a function of number of particles, respectively.

2. Experimental

To produce the nano-sized Fe particles, the pulse wire evaporation (PWE) method was used. The apparatus consists of a high voltage dc power supply, a capacitor bank, a high voltage gap switch and an evaporation chamber. A pulsed voltage of 26 kV was applied to the both ends of thin Fe wire in the chamber. Under the impulse of an electrical current during PWE, non-equilibrium overheating

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could be produced in the wire, and the Fe wire began to evaporate and then condensate into nano-clusters at its critical temperature [14].

Ethylene propylene monomer (EPM) (Kumho Chemicals, > 99%) and iron powder (DC chemical Co. Ltd., Korea, > 98.0%, c.a. 100 μm) were used as a polymer base and a micron filler, respectively. The surface of nano- and micro Fe powder was coated with low density polyethylene (LDPE) to increase the degree of dispersion of the nano-particles in the melted EPM matrix. LDPE was dissolved in an organic solvents, cyclohexane. LDPE powder (0.5 g) was dissolved in 100 ml of cyclohexane (at 110 °C) which was stirred magnetically on a hot plate. After LDPE powder was completely dissolved in cyclohexane, 5 g of Fe was added. It was then dried in the hood to obtain LDPE coated Fe powders.

Fe/EPM composites were fabricated by mixing LDPE coated Fe with EPM in the high polymer melt-mixer (Eastern Engineering, Inc.) as shown in Fig. 1(a). Fe powder and EPM pellets were pre-mixed homogeneously by using a polymer melt-mixer prior to be melted for mixing between two blades. The temperature of melted polymer was set at 190 °C, and rotation speed of the roller blades were 40 rpm. Weight concentrations of the powder in EPM were ranged from 1 wt.% to 10 wt.% for both micro- and nano-Fe. The sheet type of Fe/EPM composites were prepared by hot pressing at 190 °C and 20 MPa for 10 min. Fig. 1(b) shows photographs of 10 wt% nano- and micro-Fe reinforced EPM composite sheet. Though the color of both nano- and micro-Fe powder was black, the color of nano- and micro- Fe dispersed /EPM composite were dark black and gray, respectively.

To evaluate the morphological status and the degree of dispersion of the particles in the prepared samples, SEM and TEM images were obtained from micro-Fe/EPM and nano-Fe/EPM composites. The tensile strengths of the samples were also evaluated by ASTM D638. We examined the magnetic characteristics of micro-Fe/EPM, and nano-Fe/EPM composites by means of vibrating samples magnetometer (VSM) in this investigation.

3. Results and Discussion

Using of the PWE method, we have obtained nano-crystalline Fe particles showing a spherical shape as shown in Fig. 2. The size distributions of the produced Fe particles and surface modified Fe by LDPE were varied from 50 to 200 nm as shown in Fig. 2 taken by SEM and TEM. Fig. 2(a) shows the Fe particles synthesized by PWE, and 2 (b) and 2(c) represent the LDPE coated nanopowders. LDPE was used for a surface treatment because it has hydrophobic property, same to EPM base, which can increase the wettability and lubricancy of the

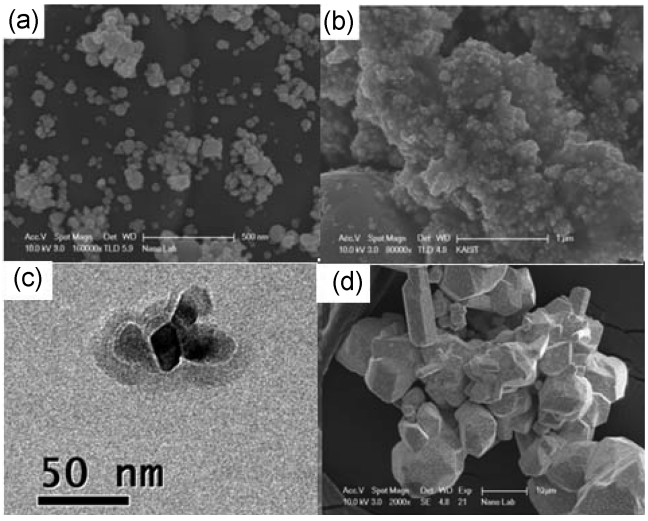

Fig. 2. (a) Fe nanoparticles synthesized by PWE, (b) LDPE coated Fe nanopowders measured by SEM, (c) LDPE coated Fe nanopowders measured by TEM, and (d) LDPE coated Fe micron powders.

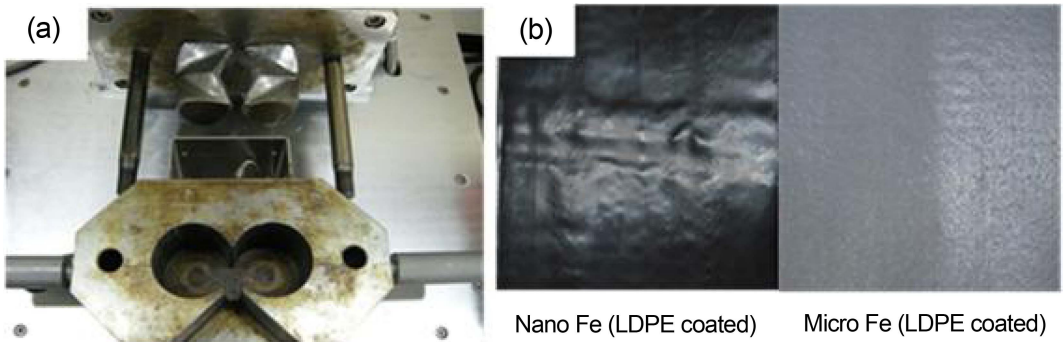

Fig. 1. (a) Polymer melt mixing roller blades, and (b) Photograph for 10 wt.% of nano-Fe and micro-Fe reinforced EPM sheets fabricated by hot-pressing.

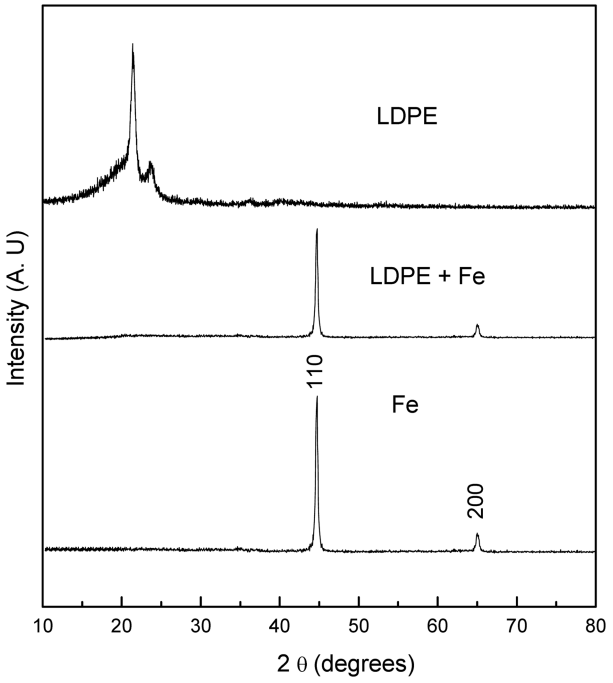

Fig. 3. XRD patterns for LDPE, LDPE coated Fe nanopowder, and Fe nanopowders prepared by PWE.

nano-particles in the polymer matrix [13]. Fig. 2(d) shows the LDPE coated commercial Fe particles with micron size.

To evaluate the LDPE coating status of the nano-Fe particles, XRD patterns were measured. Fig. 3 shows the x-ray diffraction pattern for Fe nanopowders synthesized by PWE, pure LDPE and LDPE coated Fe nanopowders. Based on the XRD patterns, the peaks for LDPE were rarely observed because the amorphous phases were generated from the crystalline structure of LPDE during dissolving and stirring in cyclohexane. Also, the ratio of LDPE on the surface of Fe particles was very low concentration.

EPM composites with the surface treated nano- and micro- Fe powders were fabricated by using polymer melt mixer. The mixing temperature was set up to 190 °C. Fig. 4 shows the SEM images for status of dispersion for both micro-Fe/LDPE particles (5 wt.%), nano-Fe/LDPE particles (5 wt.%), and nano-Fe particles (3 wt.%) in EPM matrix. The size of micro-Fe particles shown in the images (a) and (b) were bigger than 100 μm while the sizes of nano-Fe particles in (c) and (d) were in between 50~200 nm. These images indicates that the nano-Fe powder treated by the surface modifier enhance their wettability and lubricacy. Here, the good dispersion strength of both micro-and nano- Fe powders were observed. Though the micro-Fe powders were modified by the LDPE, their wettability was decreased because the large particle attributed to cracks on the linkage of polymer chains as shown in Fig. 4(d). The nano-Fe particles without LDPE layer in EPM matrix were observed in the images of Fig. 4(e) and (f). The fillers were agglomerated, and the adhesion between particle and polymer matrix was very weak. From the SEM results, it was notified that the dispersion strength of LDPE coated Fe was significantly enhanced compared to that of pure Fe without coating layer.

The tensile strength of magnetic rubber as function of doping concentration was measured. The tensile strengths of the micron-Fe dispersed rubber were decreased with increasing micron filler concentration. Whereas, nano-Fe dispersed rubbers represent slight enhancement of the tensile strengths dependent on doping concentration. Here, the different results were attributed to the size effect of the fillers. The improvement of the mechanical property of the nano-Fe dispersed rubber is an evidence of good adhesion between nanofiller and EPM matrix. Fig. 5 shows the tensile strengths as a function of Fe concentration in rubbers.

Fig. 6 shows the variation of magnetic properties for the rubbers as a function of filler concentration. The magnetic hysteresis loops measured at room temperature for 3 wt.% and 10 wt.% of Fe particle dispersed EPM were represented at Fig. 6(a) and (b), respectively. It was observed that the magnetization increases with an increase of Fe nanoparticles content. The saturation magnetization (Ms) and coercivity (Hc) for the samples were plotted against the mass fraction of the filler. The result of the Ms and Hc are dependent on both doping concentration and particle size. The distance between particles is decreased with increasing the filler concentration. Also, the reduced inter-particle spacing is caused by the smaller particles well dispersed in the medium. Though the same amount of filler is dispersed in polymer matrix, the distance between nanoparticles is closer than those between micron fillers. The magnetostatic interaction between magnetic Fe particles is enhanced due to the closer distance of the particles. The magnetization curves for 3 wt.% of micro-Fe dispersed rubber was unsaturated as shown in Fig. 6(a). In contrast, other magnetization curves (3 wt.% of nano-Fe, and 10 wt.% of nano- and micron-Fe dispersed rubbers) were fully saturated as displayed in Fig. 6(a) and (b). It is able to assume that the stray fields from each magnetic particle rarely reach to other particles because of the far inter-particle spacing between micron fillers. The value of Ms for micro-Fe dispersed rubber was higher than those for nano-filler dispersed one. The magnetic properties of nanopowders were affected by the particle

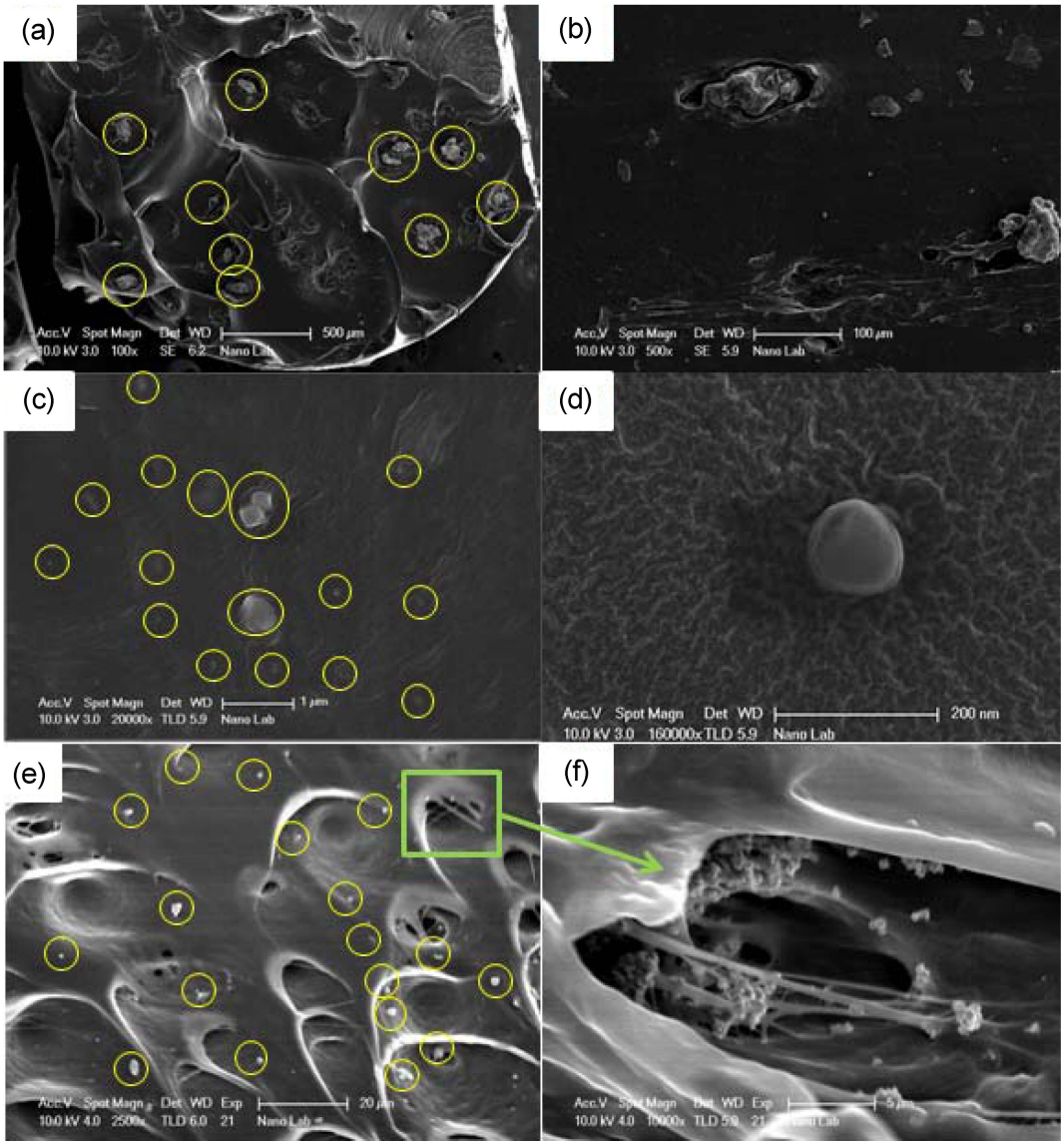

Fig. 4. The results of SEM for (a) micro-Fe/LDPE particles (5 wt.%) dispersed EPM, (b) magnified image of micro-fillers, (c) nano-Fe/LDPE particles (5 wt.%) in EPM matrix, (d) magnified image of nano-fillers with LDPE layers, (e) nano-Fe particles (5 wt.%) in EPM matrix, and (f) magnified image of nano-fillers without LDPE layers.

size resulting from anisotropy field and magnetic domain effect on the particles [11]. A typical hysteresis loop of micro-Fe (10 wt.%) dispersed rubber show a saturation magnetization (Ms) of 20.6 emu/g and coercivity (Hc) of 0.01 Oe, respectively. The value of Ms is less than 10 % of those of the bulk Fe (Ms=218 emu/g). The values of Ms for nano-Fe dispersed rubber decreased compared to those of micron filler dispersed one. This is able to explain the size effect. The magnetization is decreased with reducing the particle size due to demagnetization effect. The values of coercivity are 0.104, 0.014, and 0.096 Oe for 3 wt.% of nano- and micro-, and 10 wt.% of nano-Fe dispersed rubbers, respectively. The coercivity is affected by the particle size. The estimated single domain size of 14 nm for spherical particles with no shape anisotropy for iron is reported [15]. The coercivity depends on particle size greatly, and it is typically found that the coercivity increases with decreasing particle size, and reaches a maximum at the critical diameter of single domain about 14 nm. The value of Hc for nanofiller dispersed EPM was increased comparing with those for micron particle dispersed one.

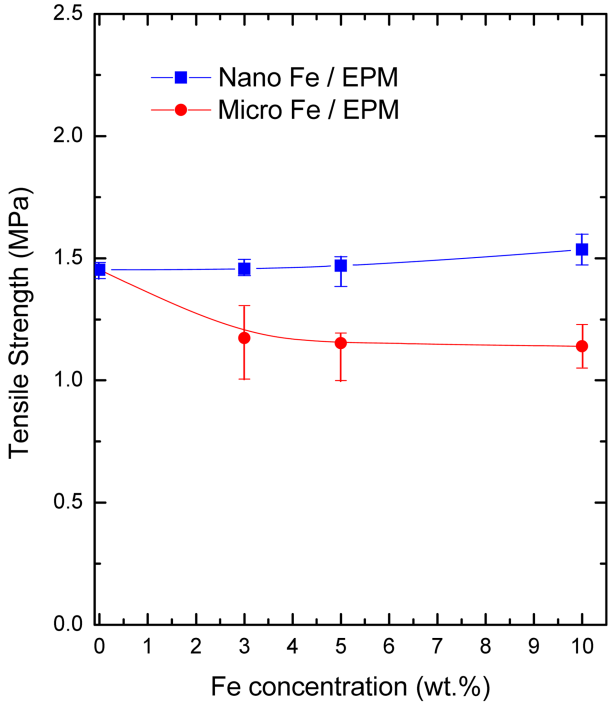

Fig. 5. Tensile strengths as a function of both nano- and micro Fe concentration in rubbers.

4. Conclusion

Nano-sized Fe powder was successfully prepared by PWE method. To enhance the dispersion strength of nano- and micro-Fe in the polymer matrix, the surfaces of the particles were treated with LDPE which was dissolved in the cyclohexane solvent. Surface treated irons were well mixed and dispersed in EPM by using a polymer melt mixer. EPM with 10 wt.% of Fe nanoparticles shows the highest of tensile strength. In this investigation, preparation of nano-sized Fe dispersed EPM was successfully performed by using an organic-solvent surface treatment method together with a polymer melt mixing process, and improvement of the mechanical and the magnetic characteristics for the nano-Fe/EPM composites were also observed.

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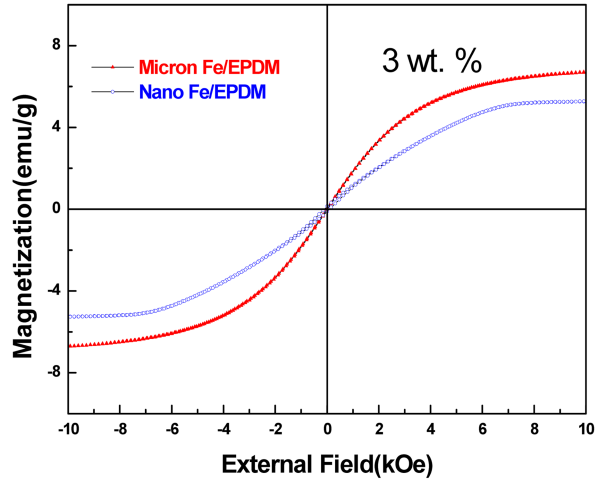
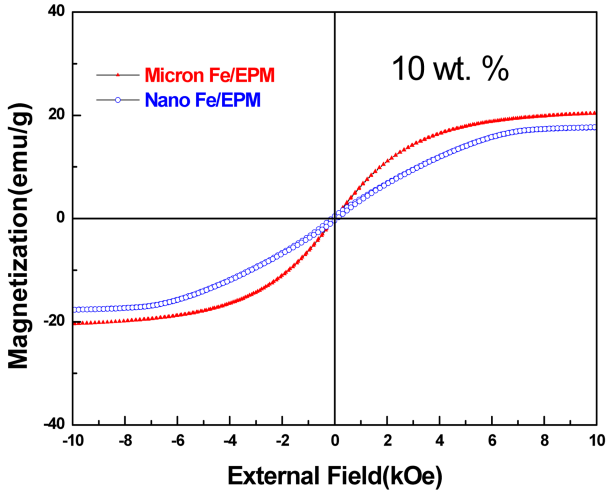


(a)



(b)

Fig. 6. Magnetic hysterisis loops measured at room temperature for (a) 3 wt.% and (b) 10 wt.% of Fe particle dispersed EPM.

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