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SHORT COMMUNICATIONS

Influence of NdFeB Fillers on Tensile and Electromagnetic Properties of Natural Rubber

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ABSTRACT

Tensile and electromagnetic properties of hard magnetic natural rubber composites were studied. In a fabrication stage, neodymium-iron-boron (NdFeB) magnets were recycled from electronic wastes, broken and then ball-milled for 1 - 3 h. The NdFeB powder was then incorporated into natural rubber (NR) by a 2-roll mill technique. Since the NdFeB powder behaved as a non-reinforced filler, thus, it inhibited cross-linking and stress-induced recrystallization. Therefore, the cure time and the tensile strength of the NdFeB-NR composites were reduced compared to the control sample without magnetic fillers. The addition of NdFeB fillers improved the electrical permittivity of NR and the magnetic moment in NdFeB-NR composites could be measured by a fluxmeter.

Keywords: Natural rubber, neodymium-iron-boron, tensile test, permittivity, magnetic moment

INTRODUCTION

In 1934, a magnetic polymer composite was first fabricated by Baermann by mixing alnico magnets with phenolic resins [1]. Since then, several types of composites have been successfully fabricated and implemented in order to combine the outstanding mechanical properties of polymers with the unique properties of the magnetic materials. Flexible permanent magnets with complex shapes can be produced by introducing ferrite fillers into elastomers such as natural rubber (NR) [2,3] and acrylonitrile butadiene rubber (NBR) [4]. Ferrite fillers are classified according to their maximum energy product or $(BH)_{max}$. Hard ferrites, used as permanent magnets, have high $(BH)_{max}$ characterized by a large area for the second quadrant of the hysteresis loop. Although ferrite rubber composites partly retain the magnetic properties of hard ferrites, there were reports about the adverse effects of magnetic fillers on the mechanical properties of rubber [2,3]. To obtain composites with improved mechanical properties with ferrite loading, epoxidized natural rubber (ENR-50) reinforced with 50 % w/w polyoxymethylene (POM) was tested as a polymer matrix [5].

Compared to hard ferrites, neodymium-iron-boron (NdFeB) is a hard magnetic material with larger $(BH)_{max}$. It is therefore widely used in hard disk drives and motors with high efficiency. NdFeB can be fabricated in forms of polymer bonded magnets by mixing with small amounts of resin [1,6]. In addition, Kokabi and co-workers [7] showed that NdFeB can be used as a filler in thermoplastic polyethylene glycol (PEG), thermosetting epoxy and elastomeric styrene butadiene rubber (SBR). Compared to traditional sintered magnets, these NdFeB polymer composites have lower cost because of the reduction in raw magnetic materials and high-temperature production steps. In this work, the feasibility of producing low-cost magnetic rubber composites is explored by using recycled NdFeB magnets and NR. Mechanical and electromagnetic properties of NdFeB-NR composites are then studied.

MATERIALS AND METHODS

Bars of NdFeB magnets removed from defunct hard disk drives were purchased from an electronic waste shop. After the removal of the protective layer, they were broken into smaller bits by a hammer and milled in a planetary ball milling machine (Retsch PM100) at 300 rpm up to 3 h. After the milling, the composition of the fine NdFeB powder was analyzed by X-ray fluorescence (XRF) spectroscopy. Selected powders with different milling times were suspended in 1-butanol in order to measure their size distribution by a laser particle size analyzer (Coulter LS230).

An air dried sheet of NR was cut into 50 g pieces. Using a 2-roll mill technique, a NdFeB-NR sample was prepared by mixing NR with carbon black (7.50 g), stearic acid (1.50 g), ZnO (2.50 g), sulfur (1.50 g), MBTS (Dibenzothiazole disulfide, 0.50 g), TMTD (Tetramethylthiuram disulfide, 0.50 g) and NdFeB (50 g) powders. A control sample was also produced without any magnetic NdFeB filler. Their cure times were measured according to ASTM D2084-2000 by an oscillating disc rheology meter (Gotech GT-7070-S2). After the samples were prepared in a compression mould using a hydraulic press (Carver, INC.) at 170 °C and die punched, the tensile test was performed according to ASTM D412-2000 using a universal testing machine (Lloyd Instruments model LR150K). To compare dielectric properties between the compounds, the permittivities were measured as a function of frequency from 1 MHz to 1.6 GHz by an RF impedance/material analyzer (Agilent 4291B) equipped with a dielectric test fixture. Magnetic moments were measured by placing samples in the core of a Helmholtz coil (Lakeshore FH-2.5) attached to a fluxmeter (Lakeshore 480).

RESULTS AND DISCUSSION

Figure 1 shows NdFeB magnets at different stages. From XRF results, the recycled NdFeB powder contained 47 % Fe and 24.76 % Nd. Other elements including O, Co, Si, Ca, Al and Pd were detected but the amount of low atomic number B could not be evaluated because of the limitation of XRF spectroscopy. The effect of the milling time on the particle size distribution of NdFeB is shown in **Figure 2**. Differential volume in the Y-axis is calculated from the volume fraction of clusters with certain diameters. Diameters of NdFeB clusters ranging from 0.04 to about 76 microns exhibit a bimodal distribution with peaks in differential volume around 2 and 25 microns. This distribution is adjusted by the milling time because of the competition between the fracturing and cold welding processes. By virtue of the cold welding [8], the clusters tend to agglomerate during prolonged milling and thus the number of smaller clusters is reduced. It follows that the average diameter increases from 13.87 to 24.47 microns with decreasing standard deviation. However, the positions of the peaks are hardly changed, implying that cold welding dominates for milling times between 1 and 3 h. Large clusters resulting from the cold welding may deteriorate the tensile strength of the composites. For this reason, the appropriate milling time for fabricating NdFeB-NR composites is 1 h or less.

(a) (b)

(c) (d)

Figure 1 Photographs of NdFeB magnets at 4 different stages: (a) a bar of a NdFeB magnet, (b) after breakage (c) after milling and (d) after mixing with NR.

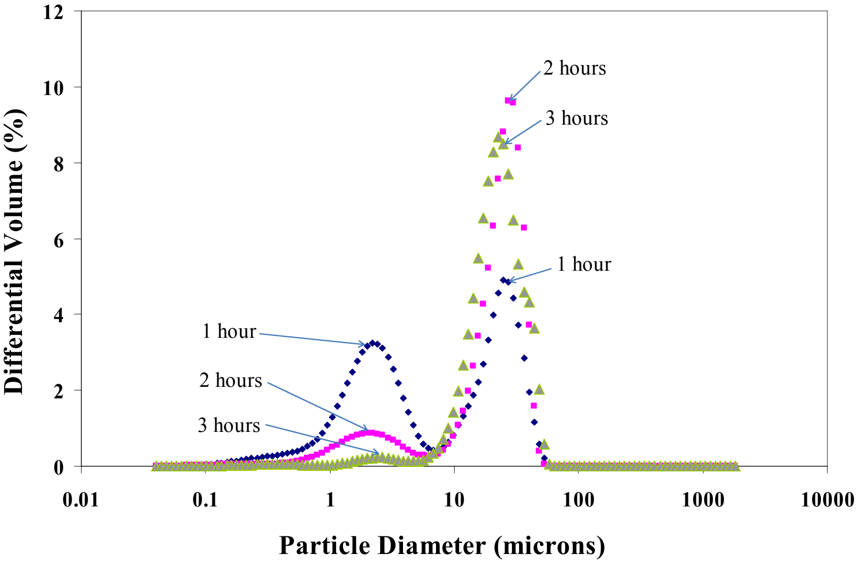

Figure 2 Size distributions of NdFeB powders after milling for 1, 2 and 3 h.

After the addition of NdFeB in NR, the micrograph of the composite in **Figure 3** shows a proper dispersion of NdFeB fillers but a rough morphology with some pits are clearly observed. Because magnetic powders act as non-reinforced fillers and affect the cross-linking process of NR [9], the cure time shown in **Table 2** is reduced by 26 s. This reason and the inhibition of stress-induced recrystallization lead to a decrease in the tensile strength by 32.15 %. Even in the case of reinforced fillers, this reduction may also occur if the NR is loaded with great amounts of fillers [10].

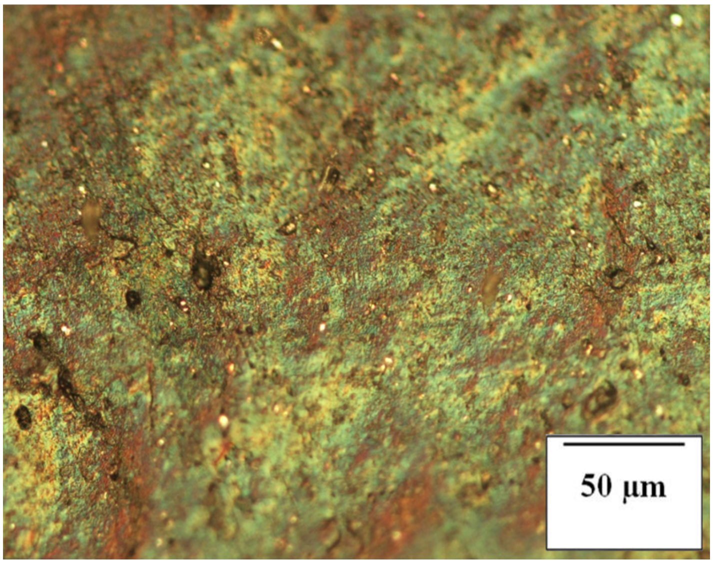

Figure 3 Optical micrograph showing morphology of the NdFeB-NR composite.

Table 2 Cure time, tensile strength and magnetic moment of NR compound without NdFeB and NdFeB-NR composites.

Parameters	NR without NdFeB	NdFeB NR composites
Cure time (s)	186	160
Tensile strength (MPa)	20.53	13.93
Magnetic moment (µWbcm)	0.008 ± 0.005	0.193 ± 0.005

From **Table 2**, magnetic moments in the order of 0.1 µWbcm can be detected in samples with NdFeB. This value is much less than the magnetic moment of bulk NdFeB magnets [7], since the milling process deteriorates the magnetic properties and the concentration of NdFeB is reduced after incorporation of NR. Nevertheless, this composite can still find applications as magnetic parts in small electromagnetic devices in which a large magnetic field is not compulsory.

Under the application of AC test signals, the electrical permittivity becomes a complex quantity. While the real part of the permittivity indicates the energy stored in the composite, the imaginary part is related to the energy dissipated in forms of heat. In **Figure 4**, the addition of NdFeB increases the real part of permittivity due to the polarization of surface charges on the metallic fillers [11]. By contrast, the imaginary part is reduced possibly due to the change in electrical conductivity by the introduction of the metallic fillers. Both real and imaginary parts are decreased with increasing frequency between 1 MHz and 1.6 GHz. This is typical for metal-dielectric composites because charges are better reoriented at lower frequencies and the polarization is therefore greater [11]. In both samples, sharp drops in the permittivity are observed at the same frequencies (e.g. 1.15 GHz) which is likely a side effect of changing measurement ranges by the RF impedance/material analyzer.

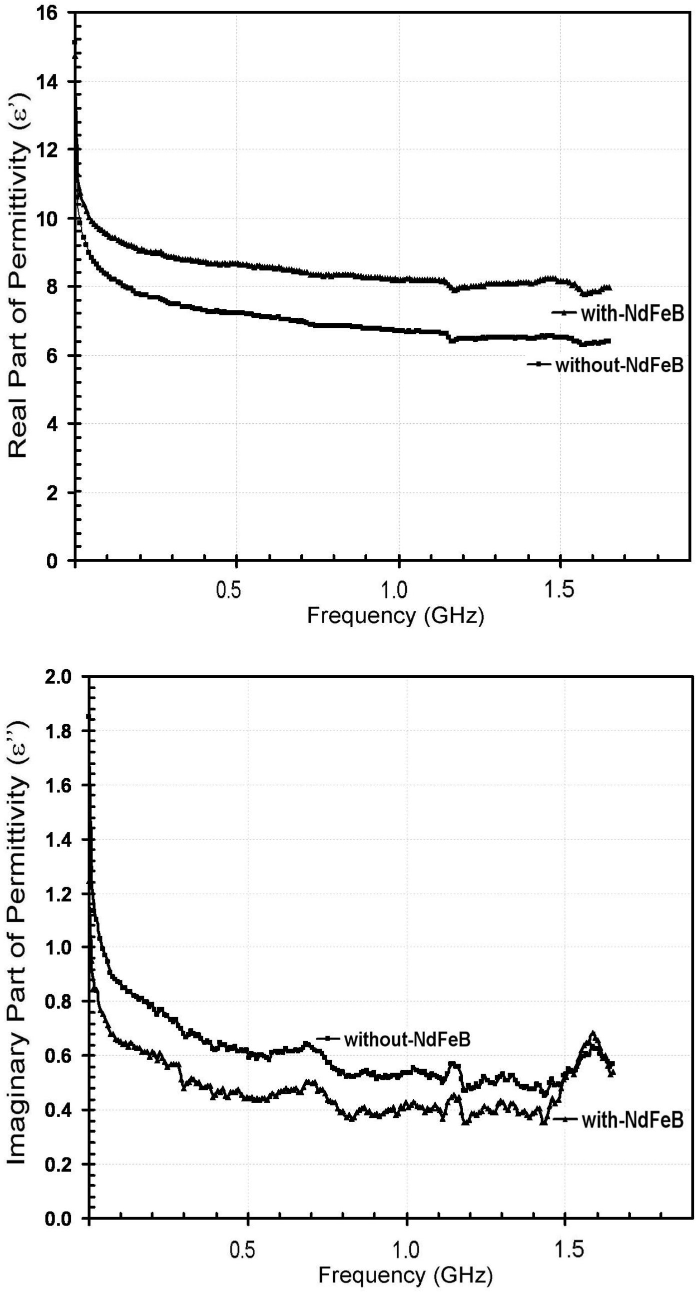

Figure 4 Complex electrical permittivity of NR without NdFeB and NdFeB-NR composites. Real and imaginary parts are shown in the top and bottom figures respectively.

CONCLUSIONS

Permanent NdFeB magnets can be recycled and used in the fabrication of magnetic rubber composite. The tensile strength and cure time of NR are decreased by the addition of non-reinforced NdFeB fillers because of the reduction in cross-linking and stress-induced recrystallization. On the other hand, dielectric and magnetic properties are improved. As a result, the composite can be implemented as light and flexible magnetic parts with different shapes and geometry. A further study has been carried out to find the optimum NdFeB loading in NR for applications.

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บทคัดย่อ

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อิทธิพลของตัวเติมแม่เหล็กนีโอดิเมียมไอรอนโบรอนต่อสมบัติการต้านทานต่อแรงดึงและแม่เหล็กไฟฟ้าของยางธรรมชาติ

งานวิจัยนี้เป็นการศึกษาสมบัติการต้านทานต่อแรงดึงและแม่เหล็กไฟฟ้าของคอมโพสิตยางธรรมชาติและแม่เหล็กถาวร โดยนำแม่เหล็กนีโอดิเมียมไอรอนโบรอนมาจากการรีไซเคิลขยะอิเล็กทรอนิกส์ ด้วยการทุบให้แตกและหมุนบดเป็นเวลา 1 - 3 ชั่วโมง จากนั้นนำผงแม่เหล็กไปผสมกับยางธรรมชาติด้วยเทคนิคลูกกลิ้งคู่ เนื่องจากผงนีโอดิเมียมไอรอนโบรอนซึ่งเป็นตัวเติมที่ไม่เสริมแรง ส่งผลกับกระบวนการครอสลิงค์และยับยั้งการจัดผลึกเนื่องจากความเค้น ทำให้เวลาในการสุกตัวของยางและความเค้นลดลง เมื่อเทียบกับตัวอย่างควบคุมที่ไม่มีตัวเติมแม่เหล็ก ในทางตรงข้ามตัวเติมนีโอดิเมียมไอรอนโบรอน เพิ่มค่าสภาพยอมทางไฟฟ้าของยางธรรมชาติ และโมเมนต์แม่เหล็กของตัวอย่างสามารถวัดได้ด้วยฟลักซ์มิเตอร์

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