Materials Research Bulletin 45 (2010) 878–881

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Effect of magnetic nanoparticles on the properties of magnetic rubber

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ARTICLE INFO

Article history:
Received 27 July 2009
Received in revised form 27 December 2009
Accepted 19 January 2010
Available online 28 January 2010

Keywords:
D. Magnetic properties
D. Magnetic structure
D. Mechanical properties
D. Surface properties

ABSTRACT

A new kind of magnetic rubber was prepared through conventional rubber mixing techniques on a two-roll mill, in which the magnetic filler was Fe_3O_4 nanoparticles and was surface modified. The effect of Fe_3O_4 nanoparticles' content on the mechanical and magnetic properties of nature rubber was further investigated. The obtained results of six different compositions for nature rubber with 0, 5, 10, 15, 20 and 25 phr of Fe_3O_4 nanoparticles were compared. It was found that the magnetic rubber has higher magnetic properties and tensile strength, comparing with unfilled nature rubber. The result suggests that when the magnetic filler is nanoparticles and surface modified, the mechanical and magnetic properties of the rubber can be synchronously improved, which is difficult to be observed in previous work.

1. Introduction

Recently, magnetic rubber (MRE) has been studied for their applications on adaptive tuned vibration absorbers, stiffness tunable mounts and suspensions, and variable impedance surfaces [1–3]. It is noticed that the performances of MRE devices are very dependent on the magnetic and mechanical properties of MRE materials, so it is crucial that the effects of magnetic particles and matrix on these properties have been studied. The matrix includes silicon rubber, natural rubber, polyurethane sealant, acrylonitrile and polybutadiene as well as their blends [4–8]. The previous studies have been shown that the effect of matrix on the magnetic and mechanical properties was slight. Contrarily, the magnetic particles determine the magnetic and mechanical characterization of MRE materials. So, there were some works reporting the effect of structure and doping content of magnetic particles on the properties of the magnetic rubber [9–13]. They show that although the magnetic properties of magnetic rubber increase with increase in doping content, the mechanical properties decrease. The result is attributed to the weak adhesion between magnetic fillers and rubber [14–17]. A prerequisite of good adhesion between filler and polymer remains the surface energy of fillers, which must be greater than or equal to the surface energy of the polymer. The virgin magnetic fillers with large size exhibit a small surface energy and are apparently unable to form strong adhesive bonds with the rubber. Surface modification and nano-size increase the surface energetics. However, there are few works to study the effect of treated magnetic nanoparticles on properties of rubber. In addition, the magnetic Fe_3O_4 particles have attracted particular interests for its strong magnetic properties, simple synthesis and its low cost [18–20].

In this study, the Fe_3O_4 nanoparticles grafted with polymer were prepared by in situ synthesis method and were doped in nature rubber. The effect of the Fe_3O_4 nanoparticles on the mechanical and magnetic properties of the rubber has been investigated in detail. These results are of great value to further improve the mechanical and magnetic properties of magnetic rubber, which can be expected to apply in damping and electromagnetic interference shielding materials.

2. Experimental

2.1. Synthesis of Fe_3O_4 nanoparticles grafted with PEG

Fe_3O_4 nanoparticles grafted with PEG were prepared by the co-precipitation of $FeCl_3{\cdot}6H_2O$ and $FeSO_4{\cdot}7H_2O$ with NaOH in the presence of PEG-6000 according to the literature [20]. Its structure was characterized by TEM and IR, suggesting that the average size of the magnetic nanoparticles is about 42.0 nm and the magnetic nanoparticles were coated by PEG.

2.2. The preparation of magnetic rubber

Ingredients of the rubber compounds were mixed on a two-roll laboratory mill of 80 mm diameter, 300 mm length, the speed of slow roll being 24 rpm and the gear ratio 1.4. The ingredients were added according to following: 100 phr nature rubber, 45 phr carbon black, 5 phr ZnO, 1 phr stearin, 2 phr MDA, 1 phr cz and

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doi:10.1016/j.materresbull.2010.01.017

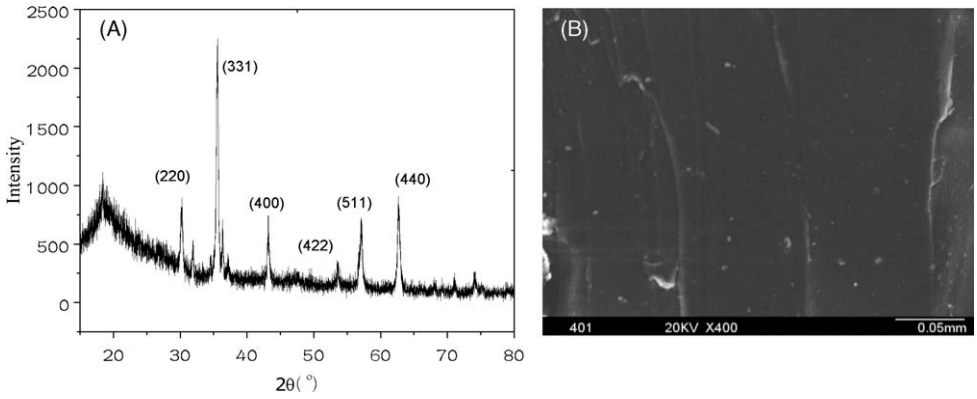

Fig. 1. (A) XRD and (B) SEM of magnetic rubber containing Fe_3O_4 nanoparticles.

3 phr sulfur. The mass fractions of the Fe_3O_4 nanoparticles in the matrix were 5–25 parts per hundred grams of rubber. For each type of rubber compounds, the vulcanization process was performed by compression molding process at 150 °C for 20 min under a pressure of approximately 10 MPa from an electrical resistance heating press.

2.3. Characterizations

Tensile tests were performed on a Universal Testing Machine (WD-5D, Chang chun, China) with a crosshead speed of 50 mm/min at 25 °C. The average of five tests is reported here.

The phase structural identification of the products were characterized by the X-ray diffraction (XRD) with Cu Kα radiation (λ = 1.54 nm) at a scan rate of 4°/min.

The structure investigations of magnetic rubber were analyzed with a Hitachi S-3500N scanning electron microscope (SEM).

TG/DTA analysis was carried out over the temperature range from 20 °C to 600 °C at 10 °C/min by means of a Perkin–Elmer Diamond instrument.

The magnetic properties were measured at room temperature using a HH-15 vibrating sample magnetometer (VSM, I_{max} = 50 Å, $P \leq 6$ kW, H_{max} = 15,000 Oe, sensibility between 4 and 5×10^{-5}), made by Nanjing University Instrument Plant.

3. Results and discussion

The formation of magnetic rubber (MRE) is confirmed by the X-ray powder diffractions as shown in Fig. 1A. It clearly shows growing parallel to (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes of cubic Fe_3O_4, indicating that the Fe_3O_4 nanoparticles have been doped into nature rubber. In addition, the average size (ca. 46.0 nm) of the Fe_3O_4 nanoparticles doped in nature rubber (NR) can be calculated according to the XRD peak of (3 3 1). It is almost same with the size (42.0 nm) of pure Fe_3O_4 nanoparticles, suggesting that the Fe_3O_4 nanoparticles have good stabilization and well dispersion in NR. The result is further determined by the SEM image as shown in Fig. 1B. There is not any agglomerate. Furthermore, the gaps between Fe_3O_4 nanoparticles and nature rubber cannot also be seen. These results indicate that the Fe_3O_4 nanoparticles can be well dispersed in the rubber matrix and has good adhesion with rubber matrix.

Thermal properties of the magnetic rubber were examined by TG/DTA as shown in Fig. 2. In this figure, a thermogram of an unfilled NR is also given for comparison with the data of magnetic rubber. The TG curve of unfilled NR (Fig. 2A) shows gradual weight loss at 200–370 °C, considerable weight loss at 370–481 °C and slight weight loss above 481 °C. Furthermore, four endothermic peaks are found at 210 °C, 270 °C, 370 °C and 481 °C on the DTA curve. Normally, an endothermic dent indicates the weight loss due to decomposition of additives and rubber. Obviously, in the presence of oxygen, the unfilled NR loses weight because of the decomposition and volatilization of additives in rubber and combustion of nature rubber at 200–481 °C, and the endothermic dent with slight weight loss above 481 °C results from thermal decomposition of nature rubber. For NR filled with 25 phr magnetic nanoparticles, there is gradual weight loss at 200–368 °C, considerable weight loss at 368–481 °C and slight weight loss above 481 °C, as can be seen in the TG curve (Fig. 2B). In the DTA curve, five endothermic peaks at 210 °C, 260 °C, 327 °C, 368 °C and 481 °C are observed. Compared with the TG/DTA characteristics of unfilled NR, it should be noticed that a new endothermic peak at 327 °C appears, which is assigned to the interaction between Fe_3O_4 particles and the matrix.

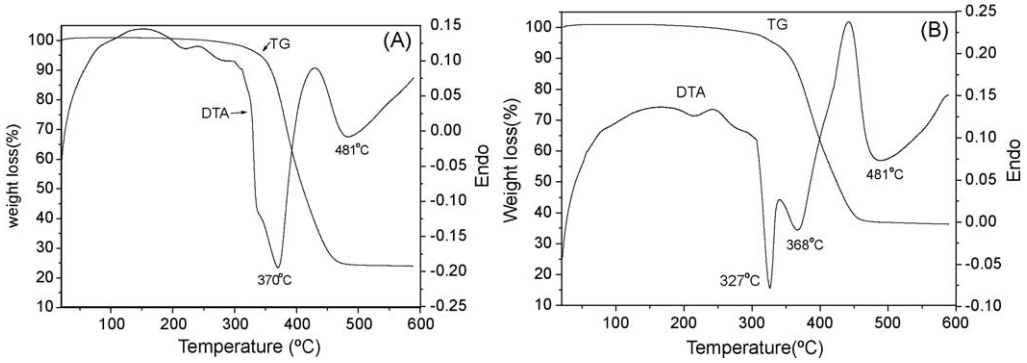

Fig. 2. TG/DTA curves of nature rubber (A) filled and (B) unfilled with Fe_3O_4 nanoparticles.