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Modified silane-coated carbonyl iron/natural rubber composite elastomer and its magnetorheological performance

Ji Su An [a], Seung Hyuk Kwon [a], Hyoung Jin Choi [a,*], Jae Heum Jung [b], Young Gil Kim [b]

[a] Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Republic of Korea
[b] Materials Development Team, Daeheung Rubber & Technology Co., Ltd., Kimhae 621-884, Republic of Korea

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ABSTRACT

To improve the dispersion of carbonyl iron (CI) particles in a rubbery medium, CI particles were pre-treated with (3-aminopropyl) triethoxy silane (APTES), and processed with natural rubber for the fabrication of magnetorheological (MR) elastomers. In particular, for its anisotropic state, the MR elastomer sample was cured under a specific magnetic field to align the magnetic particles in the direction of the magnetic field. Scanning electron microscopy and mapping analysis were carried out to observe not only the coating of the CI particles with APTES but also the anisotropic state and the dispersion of CI particles in the MR elastomers. Viscoelastic experiments, such as strain amplitude and frequency sweep tests, were measured using a rotational rheometer under a range of applied magnetic fields. The CI/APTES-based MR elastomers demonstrated superior MR properties to the CI-based MR elastomer according to the rheological tests.

1. Introduction

Magnetorheological (MR) elastomers are smart and intelligent structural materials [1,2] whose mechanical properties, such as rheological and elastic characteristics, can be tuned and modified reversibly within a few milliseconds using an external magnetic field [3–6]. Therefore, MR elastomers can have a wide range of engineering applications, including electric current active element [7], suspension bushing [8], seismic protection [9], engine mounts [10,11], and adaptively tuned vibration absorbers [12,13]. MR elastomers are generally composed of magnetizable particles in a non-magnetic matrix, such as silicone rubber [14], natural rubber [15,16], polyurethane [17], and polybutadiene rubber [18]. Among the many types of rubber, natural rubber is used widely as a matrix of MR elastomers [19]. Contrary to this solid analogue, magnetizable materials can be also dispersed in a liquid medium, such as mineral oil and silicone oil as for MR fluids [20]. These MR fluids also show a rapid and reversible change between a liquid-like and solid-like state under an applied magnetic field. On the other hand, MR elastomers overcome the disadvantages of MR fluids, such as environmental contamination, particle settling, and sealing problems by changing the fluid matrix into a solid matrix. Furthermore, MR elastomers can be fabricated in the presence or absence of an external magnetic field. Chain-like structures called anisotropic MR elastomers, are being fabricated during the cross-linking process in the presence of an applied magnetic field owing to the induced interactions between particles. On the other hand, elastomers are called isotropic MR elastomers for those cured without the application of an external magnetic field [21].

The damping property of MR elastomers depends on the types of the rubber matrix and magnetic particle as well as the interactions between the particle and rubber matrix to obtain an effective damping property. In addition, the incompatibility between the magnetic particles and matrix can cause not only poor interactions and wettability between the matrix and particles, but also a poor dispersion of particles in the matrix inducing low energy absorption [22]. Therefore, to obtain MR elastomers with better dispersity and orientation of magnetic particles in the matrix when they are processed, it is important to improve the affinity between the CI particles and the matrix through surface modification of the CI particles. Among the variety of modifications, treating the magnetic particles with silane coupling agents is considered a very cost-effective and efficient method for increasing the affinity between the magnetic particles and the matrix. Therefore, one of the silane coupling agents, (3-aminopropyl) triethoxy silane (APTES), was selected for its higher affinity through the modification of CI particles, because APTES-modified CI can enhance the affinity in the matrix [23]. Note that silica [24] and polymer [2] have been also applied for the coating of CI particles.

* Corresponding author.
E-mail address: hjchoi@inha.ac.kr (H.J. Choi).

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In this study, anisotropic MR elastomers were fabricated with magnetic particles of both CI/APTES and CI, natural rubber, and carbon black as an additive. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and mapping methods were carried out to confirm the morphology of the CI-coated APTES and CI-based MR elastomers. Various magnetic and rheological tests were performed to compare the properties of the CI and CI/APTES-based elastomers.

2. Experimental

2.1. Materials and sample preparation

Carbonyl iron (CI) particles (CC grade, BASF, Germany) with a mean particle size and density of 3–5 μm and 7.8 g/cm^3, respectively, were used as an MR active material. CI particles (500 g) were first pre-treated with 0.5 M HCl (400 ml) for 1 h to activate their surface by producing OH groups on them. The pre-treated particles were then washed several times with methanol. After pouring methanol (1400 ml) onto the pre-treated particles, the mixture was transferred to a 3-neck flask and APTES (99%, Sigma-Aldrich, USA) (17.5 ml, 16.56 g) was then added to the solution. The reaction mixture was kept stirring with 300 rpm at 60 °C for 24 h. After polymerization, the CI particles activated with APTES were washed approximately five times with methanol and dried at 60 °C for 24 h. As a result, the surface of the CI particles with amino groups (CI-NH_2) were obtained.

Both pristine CI particles and synthesized CI/APTES particles were used to prepare the MR elastomer samples, which consisted of three components: magnetic particles, carbon black (CB) (N990, Cancarb, Canada) as additives, and natural rubber (NR, CV-60) as a matrix. The recipe was 150 phr of magnetic particles, 100 phr of NR, and 20 phr of CB. Initially, magnetic particles and carbon black were mixed with natural rubber by general rubber mixing techniques using a Banbury mixer (HYB-3L, Hyupyoung machinery Co., Korea) for 15 min. The mixture was then poured into the mold. To prepare the anisotropic MR elastomer, the magnetic particles/NR composite was molded into 1.5 mm thick films at 160 °C for 400 s using the customized magnet-heat coupled device under a magnetic field with an intensity of 840 mT. The magnetic particles were aligned in the matrix according to the magnetic field so that an anisotropic MR elastomer was finally obtained.

2.2. Characterization

SEM (S-4300, Hitachi, Japan) was used to examine the morphology of the samples. After soaking these samples in liquid nitrogen, they were cut in half vertically and coated with platinum. The CI was well coated with APTES and the aligned structure of the MR particle samples in the MR elastomer matrix was obtained from the SEM image and EDS by analyzing the mapping images.

The magnetic properties of the CI-coated with APTES and pure CI were confirmed using a vibrating sample magnetometer (VSM, Model 7407, Lakeshore, U.S.A.) at room temperature.

The dimensions of the MR elastomer samples were approximately 20 mm in diameter and 1.35 mm in thickness. The rheological properties of the MR elastomer were tested using a rotational rheometer (MCR 300, Physica-Paar, Germany) with the equipment of the rheometer (MRD 180, Physica-Paar, Germany), which supplied the power for the rheometer and a parallel disc configuration with a diameter of 20 mm (PP20/MRD/TI/S) equal to the diameter of the MR elastomer samples. Because the MR elastomer samples could slip between the sample and parallel plates, sand blasted parallel disc was used to avoid potential slipping during the rheological measurement. Moreover, a constant normal force of 1N was applied to prevent further slipping. The magnetic field was applied from 0 kA/m to 343 kA/m. After each measurement, a demagnetization process was carried out to demagnetize the MR fluid fully. The MR properties were measured at room temperature from tests of the strain amplitude sweep and angular frequency sweep. Strain amplitude sweeps were defined in the range of 0.01–1% with a constant frequency of 1 Hz to examine the linear viscoelastic (LVE) region. Angular frequency sweeps were further tested from 1 to 100 rad/s with a constant strain of 0.02% in the LVE region, and the storage modulus was measured as a function of the angular frequency.

3. Results and discussion

Fig. 1 shows a schematic diagram of the functionalization of magnetic CI particles with silane. The surface of the CI particles was treated using a two-step synthetic process. At first, the OH groups were activated on the surface of the CI particles to enhance the interaction between CI and APTES by treating with HCl. Subsequently, the CI particles were functionalized with APTES (CI-NH_2) to react with the OH groups on the surface of the CI particles, and to enable further reactions by functional amino groups.

Fig. 2 presents SEM images of both pure CI and CI/APTES particles. The pure CI particles possess spherical shapes ranging in size from 3 to 5 μm (Fig. 2(a)). The size of the CI/APTES particles from their SEM image in Fig. 2(b) was slightly larger than that of the pure CI particles. The CI/APTES particles had a rough surface, whereas the pure CI particles had a smooth surface. The particles on the surface of the CI/APTES were considered to be APTES, which is adsorbed to the CI particles due to the interaction between OH groups of the surface of CI and APTES.

Fig. 3 shows SEM images of the CI and CI/APTES particles (Fig. 3 (a and c)) along with their corresponding ED spectra (Fig. 3(b and d)). EDS of the CI particles indicated that the CI particles have high contents of Fe ions (93.62 wt.%) (Fig. 3(b)). On the other hand, the CI/APTES particles contained a small content of Si ions (0.17 wt.%) along with Fe ions due to surface modification by a simple chemical method. This result confirmed that the silane group was actually attached to the surface of the CI particles.

On the other hand, Fig. 4 shows SEM and mapping images to confirm the morphology of the anisotropic MR elastomer samples, which were cut perpendicularly to the surface of the disc after immersing the MR elastomers into the liquid nitrogen. Fig. 4(c and d) show mapping images by EDS analysis. The white dots show that the Fe contents from the CI particles exist and these magnetic particles were aligned clearly to the direction of the magnetic field applied during the curing process in the matrix, as shown in Fig. 4. The effects of pre-alignment were already treated previously [16].

Fig. 5 presents the magnetic moment and hysteresis loops of CI and CI/APTES, which were obtained using a VSM as a function of the magnetic field from -10 to 10 kOe. Pure CI particles (196.33 emu/g) showed slightly higher magnetization saturation compared to that of the CI/APTES particles (186.28 emu/g) due to the compact layer of silane groups on the surface. Even if the saturation magnetization values of CI/APTES decreased slightly, the high magnetization saturation values of CI/APTES showed that these particles can be used as MR materials. The narrow hysteresis loops meant negligible remanence. Moreover, the density of CI/APTES was reduced slightly to 7.78 g/cm^3 compared to 7.80 g/cm^3 for pure CI particles.

The MR effect of the MR elastomer was obtained by measuring the dynamic modulus, with and without a magnetic field. The dynamic modulus is important to confirm its viscoelastic characterizations. Therefore, the strain amplitude sweep test and angular