On the mobility of iron particles embedded in elastomeric silicone matrix

R Rabindranath and H Böse
Fraunhofer ISC, Neunerplatz 2, 97082 Würzburg, Germany
E-mail: raman.rabindranath@isc.fraunhofer.de

Abstract. In this contribution the rheological and magnetorheological properties of different polydimethylsiloxane (PDMS) based magnetorheological elastomers (MRE) are presented and discussed. In order to investigate the mobility of the iron particles with respect to the rheological characteristics, the iron particles were silanized with vinyltrimethoxysilane to enable a reaction between the modified particle and the cross-linking agent of the silicone elastomer. In addition, the vinyl-functionalized particles were further modified by the coupling of the superficial vinyl groups with a long-chain hydride terminated PDMS, which enables a reaction pathway with the vinyl terminated PDMS. On the other hand, the iron particles were treated with surfactants such as fatty acids, calcium and aluminum soaps, respectively, prior to vulcanization in order to increase the mobility of the iron particles in the elastomeric matrix. It was found, that both, the modification with the long-chain hydride terminated PDMS as well as the treatment with surfactants lead to an increase of the storage modulus $G'$, the loss modulus $G''$ and the loss factor $\tan \delta$ in the magnetic field. It is concluded that both modifications, the coupling with long-chain hydride terminated PDMS as well as the treatment with surfactants, provide a greater mobility of the iron particles and hence a greater friction represented by the increase of the loss factor $\tan \delta$. Consequently it is assumed that untreated iron particles are less mobile in the rubber matrix due to covalent bonding with the silicone components, most likely due to the reaction of the hydroxyl groups on the metal surface with the silane groups of the cross-linking agent.

1. Introduction
Magnetorheological elastomers (MRE) represent a new class of smart materials whose rheological properties can be tuned upon exposure to an external magnetic field. MRE displays a composite material consisting of homogeneously distributed or columnar structured ferromagnetic particles embedded in a solid or gel-like, non-magnetic elastomeric matrix. The elastomeric matrix can be polyurethane, natural rubber, synthetic rubber and most of all polydimethylsiloxane [1-3]. The preparation of MRE with chain-like columnar structures requires the alignment of the ferromagnetic particles which is achieved upon exposure to a magnetic field, prior to or during the curing process.

MRE exhibit several interesting properties such as a tunable Young’s, storage and loss modulus, which render this material a suitable means for a variety of new applications. Possible applications of MRE comprise adaptive damping, vibration extinction and magnetic field induced actuation [4,5]. In order to gain a deeper understanding on the MRE concepts, which is essential for the tailoring of materials towards a specific application, the mobility of the iron particles within the elastomeric matrix.

1 Corresponding author.
matrix was investigated. For this purpose, the mobility of the magnetic particles within the elastomeric matrix was modified in two different ways. It was assumed that the modification of the particles with a surfactant increases their mobility whereas the attachments of PDMS-linker with functional groups, which enable reaction with the silicone matrix, decrease their mobility. In this study, two different industrial surfactants as well as two different PDMS-linkages were applied and the rheological properties of the MRE made thereof were compared.

2. Experimental

Vinyl-terminated PDMS, hydride-terminated PDMS, platinum-divinyltetramethyldisiloxane complex (Karstedt catalyst) and silicone were purchased from different commercial suppliers. Spherical carbonyl iron powder (CIP), type EM, was supplied by BASF. All the materials were used without further purification. The characterization was carried out on the Rheometer MCR 300 and MCR 501 from Anton Paar, Austria.

The MRE prepared in this work consist of 30 Vol.% on CIP homogenously dispersed in a home-made silicone rubber formulation. The rubber formulation consists of vinyl-terminated PDMS, hydride-functionalized cross-linker and a special plasticizer mixture in order to ensure full solubility of the surfactants. The curing, i.e. hardening process of the rubber formulation and the composite, respectively, is accomplished upon the Pt-catalyzed polyaddition at elevated temperatures using Karstedt’s catalyst. The reaction scheme of the cross-linking reaction is shown in Scheme 1.

![Scheme 1. Cross-linking reaction through Pt-catalyzed hydrosilylation.](image-url)

The modification via the silanization route of the CIP is depicted in Scheme 2. The silanization is typically carried out in pure ethanol with 1% water added under vigorous stirring of the suspended CIP over a period of six hours at room temperature. At first, the methoxy groups of vinyltrimethoxysilane are hydrolyzed in-situ under conversion into silanol groups and release of methanol. In a second step,
the silanol undergoes a condensation reaction with the hydroxyl groups on the iron surface leading to the formation of a covalent bond between the iron particle surface and the silicone compound.

![Scheme 2. Silanization of CIP with vinyltrimethoxysilane.](image)

After completion of the silanization, the CIP was simply filtered off, thoroughly washed with ethanol and dried in vacuum. One part of the vinyl-functionalized CIP was then directly processed into MRE containing 30 vol.% of modified CIP.

The other part of the vinyl-functionalized CIP was subjected to a further modification step according to Scheme 3. For this purpose, the vinyl-functionalized CIP was suspended in hexamethyldisiloxane (volatile, low molecular weight silicone oil) and was coupled with a long-chain hydride-terminated PDMS using the Pt-catalyzed hydrosilylation. The reaction was carried out under vigorous stirring with a large excess of hydride-terminated PDMS at 80°C for a period of four hours. After this period, the product was filtered off and thoroughly washed with hexamethyldisiloxane until the filtrate was free of any residues. The final product was then dried under vacuum and processed into MRE.

![Scheme 3. Modification of vinyl-functionalized CIP with long chain hydride-terminated PDMS.](image)

In contrast to the silanization procedure, the modification of CIP with surfactants is accomplished simply by adding smallest amounts of the surfactant to the rubber formulation. When adding surfactants to the rubber formulation care must be taken in the amount added. It is important to add an effective amount of surfactant for the steric shielding of the particles but the amount must not exceed a certain level at which the degree of cross-linking is altered significantly. The effect of the surfactant...
addition is displayed by a slightly reduced viscosity of the liquid rubber formulation, shown in Figure 1. In order to ensure full solubility of the surfactants, a solubilizer was incorporated into the rubber formulation. All MRE prepared in this study are based on the same rubber formulation.

3. Results and discussion

Figure 1 displays the storage modulus (G') and the loss modulus (G'') of modified and unmodified MRE in dependence on the magnetic flux density. Obviously, the dispersant-modified samples and the long-chain modified sample exhibit the same rheological behavior even though the modifications are completely different. Nevertheless, with rising magnetic flux density these modifications lead to increased values of the storage modulus and to a greater maximum of the loss modulus resulting in an increased loss factor (Figure 2).

![Figure 1. Storage modulus and loss modulus of modified and unmodified MRE samples in dependence of magnetic flux density.](image1)

![Figure 2. Loss factor of modified and unmodified MRE samples in dependence of magnetic flux density.](image2)
On the other hand, the unmodified reference sample and the vinyltrimethoxysilane-modified sample, with a short linkage to the elastomeric matrix, exhibit the same rheological behavior. It is concluded that the mobility of the iron particles in the surfactant-modified sample compares to the mobility in the long-chain modified sample, whereas the mobility in the unmodified reference sample compares to the mobility in the vinyltrimethoxysilane-modified sample. As a consequence, it has to be assumed that even the unmodified particles bond to the elastomeric matrix and hence exhibit a limited mobility comparable to the vinyltrimethoxysilane-modified particles, in which the short silicone linkage does not provide any greater freedom of movement. In reverse, the surfactant- and the long-chain modified sample do provide mobility.

![Figure 3. Schematic conditions of modified particles in MRE.](image)

While the surfactants arrange around the particle upon association of the polar surfactant head with the polar hydroxyl groups and thus preventing reaction with the elastomeric matrix, the long-chain modified particles are bond to silicone network through long, coiled and flexible PDMS chains, as schematically shown in Figure 3. As a result, both kinds of modifications lead to greater mobility of the iron particles embedded. The arrangement of initially evenly distributed iron particles of different mobility in the magnetic field is illustrated in Figure 4. While the increased storage modulus at a magnetic flux density above 400 mT is attributed to the more pronounced structuring and more dense arrangement of the particles within the magnetic field, the increased loss module represents the dissipative heat loss due the enhanced mobility resulting in greater overall friction. Furthermore, the greater mobility of these modifications results in softer MR elastomers which are revealed by the lower storage modulus without magnetic field. Due to the lower storage modulus in the pristine state and the higher storage modulus in the magnetized state the dispersant and the long-chain modified MR elastomers exhibit an enhanced increase factor in comparison with the unmodified reference sample.
In order to support the assumption that unmodified particles are bound to the elastomeric network, a common stress-strain experiment using the pure silicone rubber formulation without CIP and a MRE sample made thereof was carried out. With this experiment it is possible to assess the reinforcing properties of a filler material which is displayed by the increase of mechanical work required to break the sample. The reinforcing properties of a filler material are ascribed to the increase of the cross-linking degree due to the bond formation between filler and elastomeric network. Figure 5 shows the stress-strain behavior of the pure elastomer and the corresponding MRE made thereof. The work required to break the sample is represented by the integral of the individual curves. It is clearly shown that the incorporation of CIP leads to a significant increase of work required to break the sample.

Figure 4. Schemes of the arrangements of initially evenly distributed particles with different mobility in MRE in the magnetic field (arrow).

Figure 5. Tensile stress vs. strain of pure and iron particle filled silicone elastomer.
4. Conclusion

The incorporation of surfactants into a MRE admixture as well as the modification of CIP with long-chain hydride-terminated PDMS are suitable means to increase the mobility of the iron particles within the elastomeric matrix. The increased mobility leads to a softer material in the pristine state and to an enhanced stiffening in the magnetized state and hence, to a greater switching factor. Furthermore, it was demonstrated that unmodified CIP particles exhibit reinforcing properties towards addition cure silicones probably due to bond formation between hydroxyl groups on the metal surface and the reactive moieties of the cross-linker. This fact might be considered when designing MRE with a low loss module.

References

[1] Wu J, Gong X, Fan Y and Xia H 2010 Smart Mater. Struct. 19 105007
[2] Chen L, Gong X L, Jiang W Q, Yao J J, Deng H X and Li W H J. Mater. Sci. 42 5483-89
[3] Böse H 2007 Int. J. Mod. Phys. B 21 4790-97
[4] Ginder J M, Schlotter W F and Nichols M E 2001 Proc. SPIE p 433
[5] Böse H, Rabindranath R and Ehrlich J 2011 Proc. 12th Int. Conf. on Electro-Rheological Fluids and Magneto-Rheological Suspensions (World Scientific) pp 116-122