Magnetorheological elastomers – possibilities and limitations

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ABSTRACT

The mechanical properties of magnetorheological (MR) materials can be changed continuously, rapidly and reversibly by an applied magnetic field. Solid MR materials consist of magnetically polarisable particles, generally iron, in an elastomer matrix. The required iron concentration is high, about 30% by volume. Problems and solutions will be discussed related to MR-technology. Finally long-term properties of MR-constructions will be discussed and results from chemilumininescence measurements shown.

INTRODUCTION

Magnetorheological (MR) elastomers are controllable composites that consist of magnetically polarisable particles in an elastomer matrix and are used for e.g. vibration control and in clutch applications. MR elastomers belong to a group of smart materials that have seen an increased interest during recent years.The idea of changing the mechanicalical properties of materials by applying a magnetic field is not new. In the late 19th century viscosity change was seen when an electric field was applied across a mixture a mixture of glycerin, paraffin, and castor oil. A small and reversible change in viscosity was observed. Winslow discovered a similar but larger effect using powdered oil dispersions in 1947 (1). Winslow called the fuids "electro-viscous" (2), but the term "electrorheological" was later considered as to be more appropriate to describe the behaviour of the materials in an electric field.

At about the same time, J. Rabinow discovered a similar effect of an applied magnetic field, which he named magnetorheology (MR) (3). During the 1950´s many patents based on these phenomena, especially MR were published. However, none of them had any commercial success due to the small difference between the activated and non-activated states of the materials, coupled with sedimentation problems. The interest in ER and MR decreased. However in the 1980´s with new faster generations of computers, new applications, such as controllable dampers were made possible, and again the ER and MR seemed interesting (4). The possible applications of ER and MR fluids are numerous. For example, clutches, brakes, dampers, and shock absorbers have been suggested for both ER- and MR-fluids (5). It was long believed that that electricity was easier to use than magnetism in the theoretical modelling of the material systems (6). During the last decade the interest has shifted to MR since it has been more successful in commercial applications.

EU-PROJECTS ON MR-TECHNOLGY: INDDAMPERS
Title: Industrial novelty dampers by development of advanced materials with

high performance under electromagnetic rheological stimulation.

Contract No. G5RD-CT-1990-00125. KTH was the coordinator of this project.

In this project many possible applications were analysed. The transport sector (air, train, car) was focused on.

Crosslinked rubber to reduce the sedimentation of the heavier iron particles was chosen.

Mattias Lokander presented his licenciate thesis in 2002 (Title: Performance of isotropic magnetorheological rubber materials) and he will defend his doctoral thesis October 1 this year.

SPACE

Title: Semi active and passive control of the behaviour of structures subjected to earth quakes, wind and vibrations. The project was cordinated by Maurer und Söhne, Germany.

EU: Contract EVG1 – CT – 1999-00016. The fluid was made of iron particles in silicone oil. The sedimentation problem was solved by surface active additives together with special mixing technology.

We suceeded to stabilise bridges, chimnies etc against wind and vibrations. The project is completed and we plan to publish parts of the results in a licenciate thesis.

VASTIMAGE

Development of variable stiffness seismic isolators and vibration mitigation dampers based on magnetically controlled elastomer.

Contract EVG1-CT-2002-00063. The projectis is cordinated by Maurer und Söhne, Germany. The project is in progress and will finish in October 2005.

THEORETICAL DESCRIPTION

In figure 1 is shown idealized constitutive shear behaviour of MR fluids as a function of shear rate (left) and shear strain (right). In the absence of a field the fluids behave as Newtonian fluids. When the field is applied, they behave as Bingham bodies.

The yield stress (τ_y) of the Bingham bodies, which is field-dependent, is the most important property of these fluids.The magnetic field required to activate an MR-fluid is of order of magnitude of tenths of Tesla (5). This can be achieved with an ordinary 12V-battery. To activate an ER-fluid requires high voltage equipment (7).
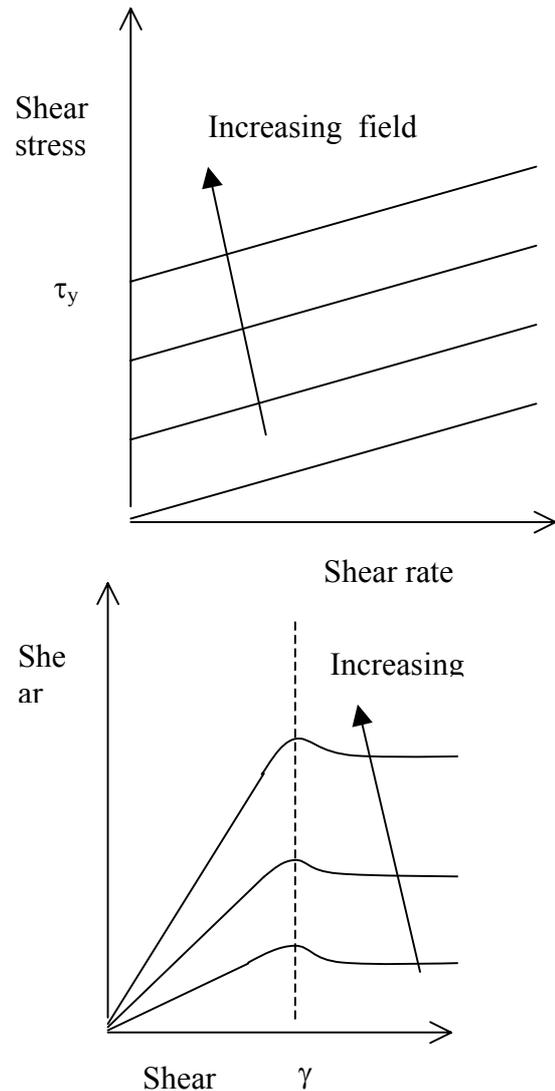
Figure 1. Idealized constitutive shear behaviour of MR fluids as a function of shear rate (left) and shear strain (right).

<u>Problems and drawbacks to be solved or handled</u>

For this type of materials problems arose in the area of degradation and stabilisation of the elastomer since polymers containing double bonds were used. These double bonds are susceptible to attack by oxygen and ozone and must therefore be protected. Among other problems to solve is to find good sensors to register accelerations. From the beginning of the projects we feared that corrosion of iron particles could be a serious problem but in the installations done during the EU-projects no such problems have appeared. Problems related to computer technology was solved and the algorithms were stable in time after the initial problems were solved. Manufacture of MR-materials demands access to good mixing equipment.

EXPERIMENTAL EQUIPMENT

The used MR-equipment is shown in Fig. 2. The magnetorheological effect was evaluated by measuring the dynamic shear modulus with and without an applied magnetic field. This was done on a double lap shear specimen, using an Instron 8032 dynamic testing machine, equipped with an electromagnet (Figure 2). The rubber segments were approximately 20×15×2 mm, and they were sandwiched between brass or steel plates. The rubber was fixed to the plates by a cyanoacrylate adhesive. The schematic equipment set-up is shown in Figure 3.

When brass plates were used as fixtures for the samples, the modulus was measured at frequencies from 1 to 21Hz. The peak-to-peak strain amplitude was 5% at 1Hz and decreased with increasing frequency down to 1.2% at 21 Hz. When a current of 20 A was used, the electromagnet was capable of applying a magnetic field of 170 kA/m through the samples between the brass plates. The resulting magnetic induction through samples containing 28% by volume of iron particles was then 0.24 T.
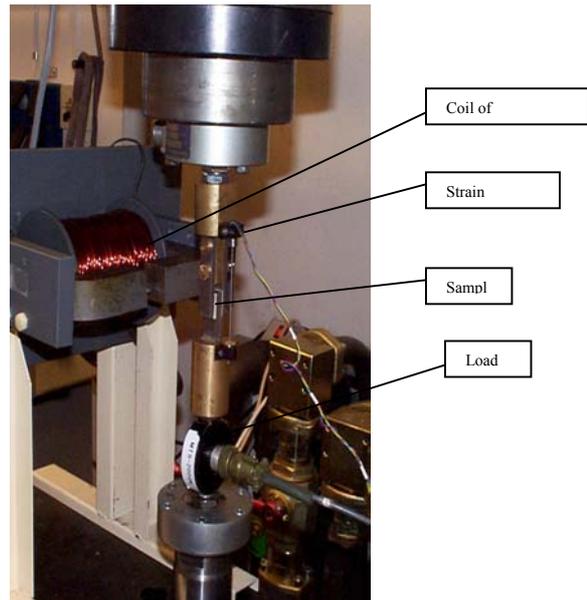
Figure 2. MR measurement equipment
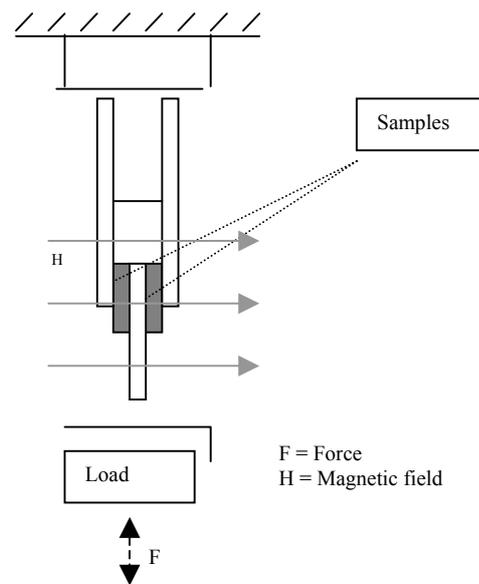
Figure 3. Schematic description of the MR-measurement equipment.

In the measurements with steel plate fixtures, the peak-to-peak strain amplitude was constant, 2%, throughout the measurement. The currents used through the coil of the magnet were 5, 2, and 1 A. These currents generated magnetic fields of 525, 280, and 130 A/m respectively, which resulted in magnetic inductions of about 0.8, 0.55, and 0.3 T through samples with

approximately 32 % by volume of iron. The magnetic fields were measured by a FH31Gaussmeter from Magnet-Physik Dr. Steingroever GmbH, Germany, and were approximately constant over the surfaces of the samples.

The modulus was first measured as a frequency sweep without any magnetic field. The measurement was then repeated with the applied magnetic field. This procedure was then repeated. Two sets of samples of each material were evaluated in this way.
To determine the amplitude dependence of the MR effect, the modulus was measured at frequencies of 2, 10, and 50 Hz, and strain amplitudes of 1.1, 2.8, 5.4, and 11 %. The modulus was measured with and without an applied magnetic field. The current through the coil during the tests with magnetic field was 5A, and the steel fixtures were used, resulting in a total magnetic induction of about 0.8 T.

Tensile test

The stress-strain properties of the materials were evaluated using an Instron 5566 tensile testing machine. The samples were "dog bones" with a cross-section of approximately 2×3 mm. The crosshead speed was 500 mm/min. Because of the varying degrees of slippage of the samples at high strains, the stress at break was considered to be a more appropriate property for comparison than the strain at break.

Rheometer measurements

The viscosity of the uncured rubber materials with zinc oxide and stearine was measured using a stress-controlled "Stresstech melt HR" rheometer from Rheologica. The oscillation frequency was 1 Hz and the stress was increased from 0.1 kPa to 10 kPa during the measurements. The rheometer was also used to measure the modulus of the cured rubber materials without iron particles, in order to evaluate the influence of the adhesive on the modulus values from the MR measurements. In these modulus measurements, the frequency was 1 to 21 Hz, as in the MR measurements.

Critical Particle Volume Concentration (CPVC)

MR solids are the solid analogue of MR fluids, where the matrix oils have been replaced by a crosslinked material such as a rubber or a gel. The most obvious advantage of an MR solid is that the particles are not able to settle, since the matrix is crosslinked. Furthermore, no container is needed to keep the material in place, and the MR effect may be slightly faster than in MR fluids since the particle does not move within the matrix. The latter is probably of minor importance since the MR effect in a fluids is also fast. However, MR solids work only in the pre-yield region, whereas MR fluids typically work in the post-yield state, and this makes the two groups of materials complementary rather than competitive. Thus, MR solids have a controllable, field-dependent modulus, whereas MR fluids have a field-dependent yield stress [5].

MATERIALS

The iron particles used were of two different types: irregularly shaped pure iron particles from Höganäs AB, Höganäs, Sweden, and spherical carbonyl iron powder (CI). Both types are pure iron particles (>99%), but they differ from each other in shape and size. The particles from Höganäs were:

ASC300 (particle size <60μm)
ASC100.29 (particle size < 180 μm)
AT40.29 (particle size ≈ 200μm).

The particle size distributions of these powders are shown in Figure 2.1. The carbonyl iron was SQ from BASF A.G., Ludwigshafen, Germany, with a particle size of 3.9 - 5.0μm.

The matrix materials used were four nitrile rubbers with different acrylonitrile (ACN) contents:
Perbunan 1845 (18% ACN)
Perbunan 3445 (34% ACN)

Krynac 45.50 (45% ACN)
Krynac 50.75 (50% ACN)

Natural rubber (SMR GP), and a mix of polybutadiene (Buna CB55) and natural rubber were used as materials with 0% ACN. All the matrix materials used, except for the natural rubber, were made by Bayer A.G., Leverkusen, Germany. The vulcanisation system used was a conventional sulphur curing system. The recipe was in all cases: 100 phr rubber, 5 phr zinc oxide (ZnO), 1 phr stearine, 1.5 phr sulphur, and 1.5 phr MBTS. In some cases, the material was plasticised, the plasticisers being di-2-ethylhexylphthalate (DEHP) in the nitrile rubbers, and hydrocarbon oil, Nytex 840 in natural rubber. The maximum plasticiser content was 17 phr, in both the nitrile and the natural rubber. The iron particles were mixed into the rubber together with the vulcanisation system in a Brabender mixer. All the materials were vulcanised at 150°C for 30 minutes under a pressure of approximately 12 MPa.

The (Critical Particle Volume Concentration) CPVC for the different powders can be calculated from their apparent densities. The apparent density of ASC300 is 2.88g cm^{-3} (Höganäs specifications). The volume concentration of

$$c_{iron} = \frac{100 \times \rho_{app}}{\rho_{iron}} = \frac{100 \times 2.88}{7.9} \approx 36.5 \text{ vol\%}$$

iron in a container with ASC300 is then:

This means that the CPVC for MR rubber materials with this iron powder is 36.5 % by volume. Similarly the CPVC for ASC100.29 is 38.2 % by volume, and for AT40.29, 38.7 % by volume.

This approach explains several of the features in our results. The maximum MR effect in the materials with ASC300 is obtained at a particle concentration of about 30 % by volume, which is close to the CPVC of this powder.
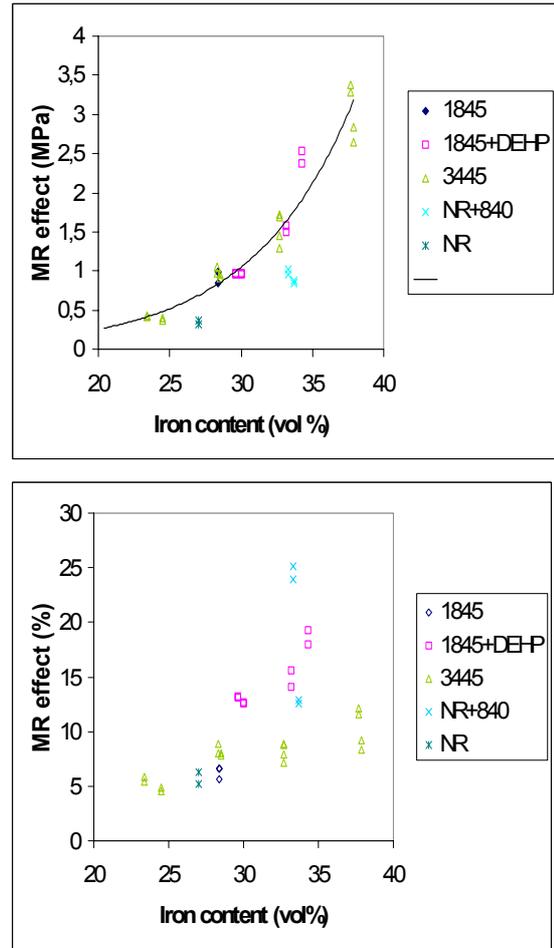
Figure 4 a Absolute MR effect
Figure 4 b Relative MR effect

At about the same concentration, the mechanical properties start to deteriorate more rapidly with increasing iron content. The shift towards lower concentrations can be explained by the fact that the dispersion of the particles is not perfect, or by the large scatter in the results from the measurements with brass plates. In the measurements with steel plates, the maximum in MR effect is closer to the calculated value of the CPVC of ASC300. The small differences in MR effect among materials with the same amounts of ASC300, ASC100.29, and AT40.29 are due to the small differences in CPVC of these powders.

With carbonyl iron, the situation is more complicated due to the tendency of these particles to form aggregates. The aggregates may look quite similar to the larger

irregularly shaped particles and the apparent density of the powder may be about the same. Nevertheless, the particles can be packed more closely together if the aggregates are destroyed. Therefore, the CPVC for materials with carbonyl iron may be larger than the values calculated from the apparent density of the powder suggest, if the particles are well dispersed in the matrix. The larger MR effect in carbonyl iron containing materials in hard matrices than in materials with the same amount of carbonyl iron in softer matrices is probably due to the fact that the particles are less well dispersed within the matrix when the viscosity is higher. Aggregates, which act like larger irregular particles, are thus present to a greater extent.

DISCUSSION

Figure 4 a shows that the absolute MR effect in isotropic MR rubbers increases exponentially with increasing iron concentration below the CPVC, regardless of the matrix material. Deviations from this behaviour, such as the slightly lower absolute MR effect in the materials with NR matrices, may be explained by local anisotropy in the samples, and differences in the degree of dispersion. Even when the term "isotropic" is used, the materials always have regions of local anisotropy. This local anisotropy may be beneficial for the MR effect if it is in the direction of the field, but it may decrease the MR effect if it is perpendicular to the field. Aggregation of particles will decrease the CPVC, the iron concentration where the MR effect is optimal. One way to determine the actual CPVC for the materials is to use electric techniques, such as volume resistivity measurements. When the concentration is high enough for the particles to form a continuous network throughout the material, i.e. at the CPVC, the electrical properties change rapidly with increasing concentration, and this makes such methods
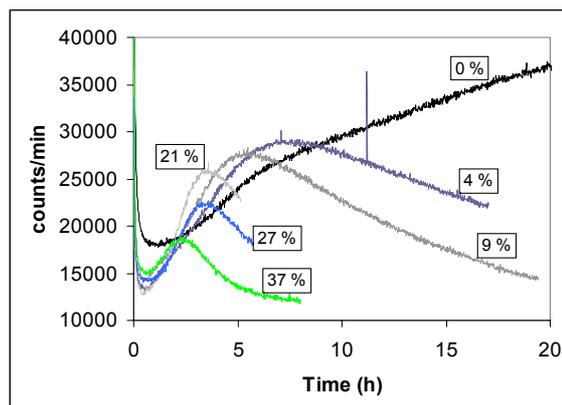
Figure 5

suitable for determining the actual CPVC for any matrix/iron particle combination [16].

The fact that the absolute MR effect is independent of the matrix material, means that softer matrix materials will increase the relative MR effect, as can be seen in figure 4 b, where the addition of plasticisers to the materials has increased the relative MR effect substantially.

These results show that, in order to achieve a large MR effect, the iron particle concentration has to be very close to the CPVC, otherwise the material becomes saturated at too low magnetic fields. It is not necessary to apply very large magnetic fields, since the MR effect does not increase much with increasing magnetic field strength when materials have started to saturate magnetically. The MR effect at about 0.8 T is only slightly larger than that at 0.5 T. A simple way to increase the relative MR effect, is to plasticise the matrix.

Longterm properties of used rubber materials
Chemiluminescence

Chemiluminescence (CL) measurements were performed on a CLD100 CL-Detector from Tohoku Electronic Industrial Co. The instrument is sensitive to wavelengths between 280 and 650 nm, with peak sensitivity in the region 400-450 nm. The measurements were performed at constant

temperature, 120°C or 90°C, with airflow of 50 ml/min through the test chamber. The sample weight was chosen so the amount of matrix material was about 3 mg.

Chemiluminescence curves at 120°C for materials with different content of ASC300 particles are shown in Figure 5

As can be seen, the time to reach the peak of the CL curve is shorter for the materials with iron. The number of counts per minute is a measure of the reaction rate, but the iron particles shields some of the light emitted, which causes the signal to be weaker when the iron content increases although the reaction is actually faster. The maximum in the CL curve corresponds to the formation of a visible oxidised skin [18].

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