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The elastic and damping properties of magnetorheological elastomers

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VTT Processes

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Abstract

Magnetorheological elastomers (MREs) belong to the group of so-called smart materials, which respond to an external stimulus by changing their viscoelastic properties. Magnetorheological (MR) material can be fluid, gel or solid material like elastomer. The mechanical properties of the MR materials change when subjected to an external magnetic field. The MREs are interesting candidates for the active stiffness and vibration control of structural systems.

The aim of this study was to increase the knowledge on the mechanical and viscoelastic properties of isotropic and aligned MREs. The focus was to clarify the changes in the elastic and vibration damping properties of both studied types of MREs when subjected to magnetic field. Another aim was to study the influence of the alignment of the magnetic particles on the composite properties with and without applied magnetic field.

Isotropic and aligned MREs were prepared from silicone elastomer matrix with varying carbonyl iron content. The MREs were tested in bending and compression modes with sinusoidal dynamic loading. The 3-point bending experiments were carried out using a dynamic mechanical analyzer (DMA) in resonance for both isotropic and aligned MREs where the filler content varied from 0 to 30 vol.%. For characterizing the materials in compression with applied magnetic field, a special coil device was designed. Isotropic and aligned MREs with 30 vol.% of Fe were also characterized in dynamic compression with varying frequencies and strain amplitudes. The spring constant, elastic/shear modulus and damping ratio/loss factor values were calculated on the basis of the measured data with and without applied magnetic field.

The stiffness and damping properties of both isotropic and aligned MREs can be modified by applying external magnetic field. In isotropic MREs the stiffness and damping increase in the magnetic field if the filler volume fraction exceeds 15 %. The damping also increases with the increasing volume fraction of iron and it has a maximum value at 27 vol.% when measured with applied magnetic field. The damping and stiffness properties of aligned MREs depend on the mutual directions of load, magnetic field and the particle alignment in the composite. If the dynamic load in bending or in compression is applied in the direction of the particle chains, the damping is initially high and the increasing magnetic field strength has only small influence on damping. In this case, dynamic stiffness is also high and can be increased by applying the magnetic field. If the external load is applied so that the deformation is concentrated in the areas between the particle chains, the damping is initially comparable to that of isotropic MREs and can be increased in the magnetic field. In this case the dynamic stiffness is quite low and applied magnetic field does not increase it significantly.

The particle network structure of aligned MREs has a significant influence on the elastic and damping properties of the composite material. Inside the chains the effective filler content is higher than the average filler content. This is due to the "trapped" elastomer captured between the particles and to the formation of the "third phase" (elastomer shell) in the immediate vicinity of the filler particle. By optimizing the particle density and alignment, either the stiffness or the damping of MREs can be increased by applying the magnetic field.

Preface

This work was carried out at the Finnish Technical Research Centre (VTT) during the period of 2001–2005. The research was initiated in a VTT internal project comprising smart materials and was continued later in a project financed by VTT and the National Technology Agency, TEKES. Important part of the study was also carried out in Los Alamos National Laboratory, New Mexico, USA during the period of August 2003 – July 2004. VTT Processes and Los Alamos National Laboratory financed this work. The study was carried out under the guidance of Laboratory Fellow, Dr. Ricardo Schwartz to whom I want to express my sincere gratitude for his profound guidance, encouragement and support. I also want to thank Dr. Douglas Safarik for all the help, suggestions and interesting discussions. Professor Tuomo Tiainen from the Institute of Materials Science, Tampere University of Technology is acknowledged for his guidance, support and valuable comments during the whole period of studies of materials science and this research work.

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My special thanks belong to my friends and family (thanks for keeping my feet on the ground), but especially to my husband Pasi for the love, support and encouragement.

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Contents

List of symbols

a	particle radius
a_m	material parameter (Eq. (4))
B	magnetic induction
b	viscous damping constant
b_c	critical viscous damping constant
b_m	material parameter (Eq. (4))
c_{11}	longitudinal modulus
c_{12}	elastic constant
c_{44}	shear constant
c_{ij}	elastic stiffness tensor
D	area captured inside the hysteresis loop
d	particle diameter
d_c	separation between the particle chains
E	Young's modulus
E_0	Young's modulus for unfilled material
E_{12}	interaction energy between the magnetic dipoles $\vec{m}_1$ and $\vec{m}_2$
e_z	unit vector

F_d	damping force
F_i	force of inertia
F_m	magnetic force
F_s	elastic spring force
F_{dyn}	dynamic force
F_{stat}	static force
F_0	external force
f	frequency
$G(0)$	zero-field shear modulus
G	shear modulus
G_0	shear modulus of unfilled material
G'	shear storage modulus
G''	shear loss modulus
$G*$	shear complex modulus
G_{ran}	shear modulus of isotropic filled material
H	magnetic field strength
h	gap between particles in a chain
h_s	sample height
K	bulk modulus

k	spring constant
k_m	factor of magnetic interaction between adjacent chains
L	fibre length
L_s	sample length
M_p	particle magnetization
M_s	saturation magnetization
m	effective mass
$\vec{m}$	dipole moment
N	number of particles
N_c	number of chains
R	particle radius
r	distance between dipoles
r_0	initial distance between the dipoles
S	unit section of the material
T	temperature
T_g	glass transition temperature
t	cycle time
w_s	sample width

z	displacement amplitude
z_0	maximum displacement amplitude
z_r	maximum displacement amplitude in resonance
β	frequency ratio
χ	magnetic susceptibility
δ	phase angle
$\tan \delta$	loss angle
ΔG	change in shear modulus
$\Delta \sigma_i$	change in initial stress
ε	strain
ε_0	maximum amplitude of strain
ϕ	filler volume fraction
ϕ_{eff}	effective filler volume fraction
ϕ_{max}	maximum filler volume fraction for cubical packing
γ	shear strain
$\dot{\gamma}$	shear rate
η	damping factor, loss factor
η_p	plastic viscosity

$\eta(\dot{\gamma})$	shear rate dependent viscosity
λ	Lamé constant
λ_w	wave length
λ_i	extension ratio
μ	permeability
μ_0	permeability of free space
ν	Poisson's ratio
ξ	damping ratio
ρ	density
ρ_{app}	apparent density
σ	stress
σ_f	stress in the fibre
σ_H	magnetic stress
σ_i	initial stress
σ_0	maximum stress amplitude
τ	shear stress
τ_y	field dependent yield strength
υ	longitudinal sound velocity in the material
ω	angular frequency

ω_0	resonance frequency, natural frequency
CPVC	critical particle volume fraction
DMA, DMTA	dynamic mechanical analyzer
e.m.f.	electro-magnetic field
ER	electrorheological
MR	magnetorheological
MRE	magnetorheological elastomer
MRF	magnetorheological fluid
NR	natural rubber
PDMS	polydimethylsiloxane
RTV	room temperature vulcanizing
SEBS	styrene ethylene butylene styrene elastomer
SDOF	single degree of freedom system
SEM	scanning electron microscopy
TVA	tuneable vibration absorber

Magnetic field strength (H)

The strength of a magnetic field generated by electrical currents outside the material, either from a solenoid or electromagnet, or from permanent magnet.

Magnetic induction (B)

When a magnetic field *H* has been generated in a medium by a current, in accordance with Ampère's law, the response of the medium is its magnetic induction *B*, also sometimes called the flux density.

1 Oersted = 79.58 Am^{-1}

1 Tesla = 795.8 kAm^{-1}

1. Introduction

Magnetorheological (MR) fluids, foams and elastomers comprise a class of smart materials whose rheological properties can be controlled rapidly and reversibly by the application of an external magnetic field. Smart materials can respond to changes in their environment and actively alter some physical or chemical property according to the change. Such materials can be utilized in devices or they can be incorporated in traditional composites to form smart composite structures, whose continuum magnetorheological response can be actively controlled in real-time [1].

MR materials typically consist of micron-sized magnetic particles suspended in a non-magnetic matrix. The magnetic interactions between particles in these composites depend on the magnetization orientation of each particle and on their spatial relationship, coupling the magnetic and strain fields in these materials and giving rise to a number of interesting magnetomechanical phenomena. MR materials include MR fluids, foams, gels and elastomers [1].

In MR fluids iron particles are suspended in a liquid carrier fluid. The flow or shear properties are controlled by the application of an external magnetic field. The interaction between the induced dipoles causes the particles to form columnar structures, thereby increasing the viscosity of the fluid. However, due to the large density difference between the liquid and the particles, gravitational settling or centrifugal separation can occur in MR fluids [1]. The flow or shear properties of MR fluids are easily controlled to enable a variety of unique torque transfer or vibration control devices. MR foams, in which the controllable fluid is contained in an absorptive matrix or magnetic particles are dispersed in a foam-like matrix, are solid-state materials with very low intrinsic modulus. MR elastomers are solid, rubber-like materials whose stiffness can be controlled to provide tuneable or adjustable mounts and suspension devices. The applications that can benefit from materials whose rheology can be continuously, rapidly and reversibly varied are numerous [1–3, 5].

MR elastomers (MRE) are composites where magnetic particles are suspended in a non-magnetic solid or gel-like matrix. The particles inside the elastomer can be homogeneously distributed or they can be grouped (e.g. into chain-like

columnar structures). To produce an aligned particle structure, the magnetic field is applied to the polymer composite during crosslinking so that the columnar structures can form and become locked in place upon the final cure. This kind of processing imparts special anisotropic properties to the viscoelastic materials. Only recently has the field responsiveness of the viscoelastic properties of these elastomers been explored [1–7, 9–14, 25–28, 30, 31, 39–41].

The mechanical and rheological properties of an elastomeric material containing magnetizable particles can be changed reversibly by applying an external magnetic field. This is called the magnetorheological effect. The origin of the field dependence of the MRE properties is the existence of field-induced dipole magnetic forces between the particles. Therefore, the mechanical behavior of MR elastomer is a combination of matrix properties and the properties of magnetizable particle formations inside the matrix. If the particles are ferromagnetic and have a net moment, the formation of columnar particle structures within the elastomer corresponds to a low dipolar energy state. Shearing of the cured composite in the presence of a field causes particle displacement from this low energy state and requires thereby additional work. In principle, this required additional work increases monotonically with the applied field, thus resulting in a field dependent shear modulus [1–7, 9–14, 25–28, 30, 31, 39–41].

MR elastomers include a wide variety of non-magnetic matrices, like natural and synthetic rubbers, silicones and polyurethanes with a varying filler volume fraction. Structurally, they can be thought as solid analogs of MR fluids and the physical phenomena responsible for the field sensitivity of these elastomers are very similar. However, there are some distinct differences in the way by which these two classes of materials are typically intended to operate. The most noteworthy difference is that the particle chains within the elastomer composite are intended to always operate in the pre-yield regime while MR fluids typically operate in the post-yield continuous shear or flow regime. This makes the two groups of materials complementary rather than competitive to each other. The strength of MR fluids is characterized by their field dependent yield stress while the strength of MR elastomers is typically characterized by their field dependent modulus [1–7, 9–14, 25–28, 30, 31, 39–41].

MR elastomers form an interesting group of smart materials with a complicated composite structure. The properties of MREs are not yet as well known as the properties of MR fluids. Aligned MREs are shown to have a field dependent shear modulus, but the other elastic properties are still quite unexplored, especially when the MREs are measured without the applied magnetic field. It is suggested that the MREs could possibly have applications in vibration damping but also the vibration damping properties have been studied only briefly [3, 7, 9, 10, 13, 14, 28, 40, 41]. This literature review is a state-of-art in MRE research, covering the existing theories, models and experimental research. For comparative purposes, the properties of MR fluids and foams are covered briefly as well.

2. Magnetorheological fluids and foams

The initial discovery and development of MR fluids and devices can be credited to Jacob Rabinov at the US National Bureau of Standards (1948), but his work was almost concurrent with Winslow's [42] work on electrorheological (ER) fluids. He introduced the concept of controlling the viscosity of an electro-viscous fluid by the use of an electric field. However, after the initial discover of Rabinov, not much information had been published on MR fluids until recently. During the past three decades, fundamental and applied research has been going on concerning the MR materials. Research efforts are now paying off – there are several commercial MR fluids and devices available [1, 35, 38].

A MR fluid has typically high concentration of magnetizable particles in a non-magnetic medium. Differences in particle size and composition result in distinct behavioral differences. Particle sizes typically range from 0.1 to 10 μm and particle volume fractions are between 10 and 50%. In MR fluids, the interaction between the magnetically induced dipoles causes the particles to form columnar structures, roughly parallel to the applied field. These chain-like structures restrict the flow of the fluid, thereby increasing its viscosity. The configuration and rigidity of these structures will depend upon several factors including the strength and distribution of the applied magnetic field, volume fraction and distribution of magnetic particles etc. The mechanical energy needed to deform these chain-like structures increases as the applied magnetic field strength increases resulting in a field-dependent yield stress. Small particle size can prevent sedimentation, but on the other hand the yield stress increases with increasing particle size [1, 3, 37, 38].

The carrier fluids are typically selected on the basis of their rheological and tribological properties and on their temperature stability. Typically petroleum based oils, silicone, mineral oils, polyesters, polyethers, water, synthetic hydrocarbon oils etc. are used. Polar liquids such as triethylene glycol, diethylene glycol methyl ether, hexyl and cyclohexyl acetate, methyl propionate and others have also been used. MR fluids often contain other additives to provide additional lubricating properties, as well as additives that inhibit particle sedimentation and agglomeration. Sedimentation is typically controlled by the use of thixotropic agents and surfactants such as xantham gum, silica gel,

stearates and carboxylic acids. The thixotropic networks disrupt flow at ultralow shear rates (the viscosity becomes nearly infinite) but the viscosity decreases as the shear rate is increased. Stearates form a network of swollen strands when used in conjunction with mineral oils and synthetic esters that serve to entrap particles and immobilize them. Fine carbon fibers have also been used for building viscosity through physical entanglement but they exhibit shear thinning due to shear-induced alignment [1, 38].

MR foam devices contain MR fluid that is constrained by capillary action in an absorbent matrix such as sponge, open-cell foam, felt of fabric. The absorbent matrix serves to keep the MR fluid located in the active region of the device between the poles by which the magnetic field is applied. The absorbent matrix requires only a minimum volume of MR fluid that is operated in a direct shear mode without the need for seals, bearings or precision mechanical tolerances. The absorbent matrix is normally attached to one of the poles. Application of a magnetic field causes the MR fluid in the matrix to develop yield strength and resist deformation [1].

Due to the open structure, the geometry of a MR fluid foam device is much less constrained than that of a normal controllable MR fluid device and multiple degrees of freedom are easily accommodated. MR fluid foam devices are highly robust and particularly suitable for low to medium force applications where a high dynamic range is desired. Fluids in these devices are resistant to gravitational settling due to the wicking action of the matrix [1].

2.1 Physical properties of MR fluids

MR fluids exhibit dynamic yield strength values in excess of 50 MPa for applied magnetic field strength values of 150–250 kAm^{-1} and values over 100 MPa at saturation. The off-state viscosity for MR fluids is generally in the range of 0.10–1.0 Pas at 25°C. The ultimate strength of MR fluids is limited by magnetic saturation of the particles suspended in the fluid. Typical MR fluid properties are given in Table 1.

Operational temperatures for MR fluids range from -40°C to +150°C. The increasing viscosity of the carrier fluid limits the minimum temperatures and the

maximum temperatures are generally limited by the volatility properties of the carrier fluid rather than the details of the polarization mechanism. Unlike in ER fluids, dissipative electric currents and joule energy loss in MR fluids are not a concern. For operating the MR fluids, both permanent magnets and electromagnets can be used [1, 3, 35, 38].

Table 1. Typical MR fluid properties [1, 3].

Property:	*Typical value:*
Maximum yield strength, $\tau_{y \text{ (field)}}$	50–100 MPa
Maximum field strength	$\sim 250 \text{ kAm}^{-1}$ (0.3 Tesla)
Plastic viscosity, η_p	0.1–1.0 Pas
Operable temperature range	-40°C to +150°C (limited by a carrier fluid)
Contaminants	Unaffected by most impurities
Response time	< milliseconds
Density	3–4 g/cm^3
$\eta_p / \tau_y^2 \text{ (field)}$, figure of merit[*)]	10^{-10}–10^{-11} s/Pa
Maximum energy density	0.1 J/cm^3
Power supply (typical)	2–25 V @ 1–2 A (2–50 watts)

*) The factor $\eta_p / \tau_y^2 \text{ (field)}$ is a figure of merit useful in estimating how large a given MR fluid device must be in order to achieve the specified level of performance. The minimum volume of active fluid in a device is proportional to this factor [1].

MR fluids are not highly sensitive to contaminants or impurities, which are commonly encountered during manufacture and usage. Furthermore, as the magnetic polarization mechanism is not affected by the surface chemistry of surfactants and additives, it is relatively straightforward to stabilize MR fluids against particle-liquid separation in spite of large density mismatch. Most MR fluids are quite dense with their density in the range of 3–4 g/cm^3 due to their high content of iron particles [1].

There are some restrictions in the use of MR fluids. Due to the high loading with dense iron particles, MR fluids are heavy. In weight sensitive applications this fact should be considered. In many rotary applications the centrifugal effects are a concern. Due to the large density difference between particles and liquid, centrifugal separation can occur at high rotational speeds. Particle and fluid density mismatch can lead to gravitational settling, but with suitable surfactants and additives long-term stability with little or no sedimentation is achievable [1].

2.2 Field-responsive behavior of MR fluids

The standard model for the particle arrangement of MR fluids under the magnetic field is based on a cubic network of infinite chains of particles aligned in the direction of the field. When the material is strained, these chains are deformed with the strain. The interparticle distance in any pair of neighbours in the chains is assumed to be the same and it increases at the same rate with the strain. In reality, the particle structure forming in the magnetic field is much more complicated consisting of cylinder-like aggregates etc. but the standard model gives a good prediction of the yield strength [38].

Experimental results have confirmed that in the presence of a magnetic field the MR fluids exhibit both a pre-yield regime, characterized by an elastic response, and a post-yield regime, characterized by a viscous response. The yield strength τ_y is used for measuring the shear strength of the particle structure formed by the application of the field [1, 3, 38]. The field-responsive behavior of MR fluids is often represented as that of a Bingham -type plastic having variable yield strength. For shear stresses τ above the field dependent yield strength τ_y, the flow under steady shear is governed by Bingham's equation:

$$\tau = \tau_y \, \eta \, (\dot{\gamma} \,), \quad \tau > \tau_y \tag{1}$$

where $\eta(\dot{\gamma})$ is the shear rate dependent viscosity. Below the yield strength τ_y (at the strains of the order of 10^{-3}), the material behaves viscoelastically:

$$\tau = G^* \, \dot{\gamma}, \quad \tau < \tau_y \tag{2}$$

where $\dot{\gamma}$ is the shear rate and G^* is the complex shear modulus. In addition to yield strength, the complex modulus also depends on the average magnetic induction. The field dependence of the yield strength is usually represented by a power law of the type $\tau_y \sim H^n$ with $1 < n < 2$. The case $n = 2$ represents the case of a linearly magnetic material [38].

While the Bingham plastic model is useful in the design and characterization of controllable fluid-based devices, true controllable fluid behavior exhibits some significant deviations from this model. One significant deviation involves the non-Newtonian behavior of controllable fluids in the absence of field [1, 35, 38]. An ideal Newtonian fluid would have a constant shear viscosity, independent on the deformation rate, and an extensional viscosity equal to three times the shear viscosity [33]. Extensional viscosity is a measure of the resistance to the pull placed on the fluid; it tells how difficult it is to stretch a thread of fluid. At a constant stretching rate, the resistance of the fluid to the pull placed on it is equal to the stretching rate multiplied by the extensional viscosity. The MR fluid pre-yield behavior is linearly viscoelastic up to 0.1% shear strain and nonlinear above this 0.1% shear strain [28].

The viscosity in the absence of a field depends on the type of the carrier fluid, suspension agents and particle loading. Due to the influence of suspension agents and changes in particle arrangement during the shear, most MR fluids exhibit significant shear thinning. If viscosity is a function of the rate of shear, a decrease of the viscosity with increasing shear rate is called shear thinning [1].

The field strength response of two commercial MR fluids is shown in Fig. 1. This shear stress data was measured at relatively low shear rates and thus it approximates the fluid yield stress as defined in Eq. (1). At low and intermediate field strength values, MR fluids are seen to exhibit sub-quadratic behavior ($1 < n < 2$) and the power law exponent can be approximated by $n \approx 1.75$. This subquadratic behavior is attributed to gradual magnetic saturation of particles with increasing field strength and the magnetorheological models predict it. Above the magnetic field strength values of 0.1 Tesla, the effects of bulk magnetic saturation are revealed as a deviation from power law behavior. The response of yield stress to the field strength levels out as the MR fluids approach complete magnetic saturation. When the particle magnetization is completely saturated, the shear stresses are nearly independent on the average magnetic induction [35]. Simple

theory predicts that the ultimate yield stress of MR fluids is proportional to ϕM_s^2 where the particle volume fraction is ϕ and M_s is the particle saturation magnetization. For pure iron, the saturation magnetization is about 2 Tesla [1].
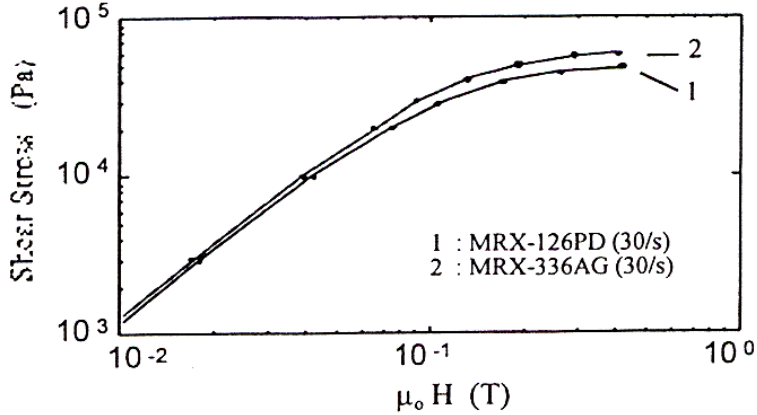
Figure 1. Shear stress vs. applied magnetic field strength μ_0H for two commercial MR fluids [1].

The magnetic induction curves for two commercial MR fluids are shown in Fig. 2. The MR fluids exhibit approximately linear magnetic properties up to the applied field strength of about 0.02 /μ_0 Am^{-1}. ($\mu_0 = 4\pi e^{-7}$ Tesla-mA^{-1} is the permeability of free space). In this region, the permeabilities are relatively constant and at the level of approximately 5 to 9 times that of the free space. MR fluids begin to exhibit gradual magnetic saturation beyond that linear regime. Complete saturation typically occurs at field strength values above 0.4/ μ_0 Am^{-1}. The intrinsic induction or polarization density ($B - \mu_0 H$) of MR fluids at complete saturation is ϕM_s . Little or no hysteresis can be observed in the induction curves. This, so-called superparamagnetic behavior is a consequence of the magnetically soft properties of the pure iron used as particulate material and of the mobility of this particulate phase [1].

Figure 2. Magnetic properties (flux density B *vs. applied field strength* μ_0H*) of two commercial MR fluids [1].*

3. Magnetorheological elastomers (MRE)

MR elastomers include a wide variety of composite materials, which typically consist of magnetically polarizable particles in a non-magnetic solid or gel-like medium. Particles inside the 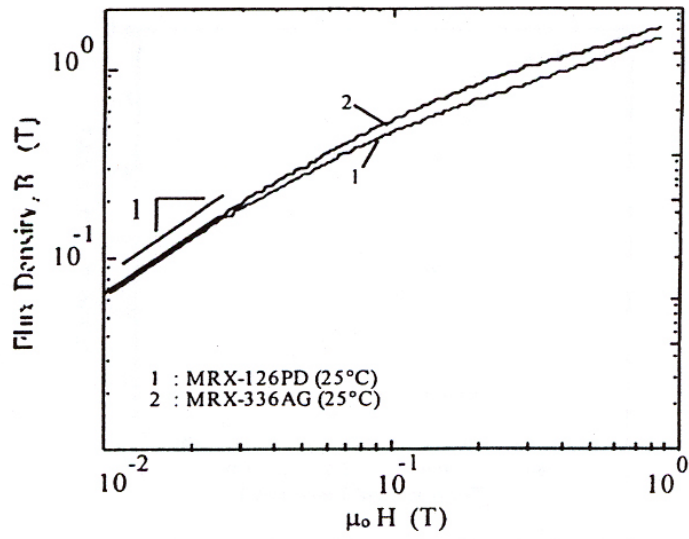elastomer or gel can be homogeneously distributed or they can be grouped to form chain-like columnar structures. In order to produce an aligned structure, magnetic field is applied to the polymer composite during crosslinking so that columnar particle structures form and become locked in their place upon the final cure. If no external magnetic field is applied during the curing, the structure of a MRE can be considered as isotropic [1–7, 9–14, 25–28, 30, 31, 39–41].

In behavior the MR elastomers are quite analogous to MR fluids. The main difference in the mechanical behavior is that solid MREs are shown to have a controllable, field-dependent shear modulus while MR fluids have a field-dependent yield stress. In addition, the obvious advantages for using solid matrix materials instead of liquids are that the particles are not able to settle with time and that there is no need for containers to keep the MR material in place [6]. In the following, the properties of the MREs are studied in more detail.

3.1 MRE as a polymer composite

When an elastomer (macro) molecule interacts with a filler particle, the effects are taking place at a nanometer scale in regions, which can be called the elastomer-filler mesophase. Elastomer compounds are highly complex polymer systems where various solid and liquid ingredients are dispersed in an elastomer matrix that by nature exhibits a strong viscoelastic character [33].

A typical MRE consists of viscoelastic materials, powdery solids (metals) and viscous liquids. All these have either a zero or limited mutual solubility or compatibility, even if they can be thoroughly dispersed in each other. The interaction between the matrix and the filler particles can be either strong or weak and it will influence the rheological and mechanical properties of the composite. Rheological experiments reveal that the linear viscoelastic region disappears with increasing filler content, which is a general characteristic of

most practical rubber compounds. Above definite filler content, the linear behavior is lost and the composites exhibit a modulus drop similar to the Payne effect. The Payne effect is defined as the decrease of the storage or in-phase shear modulus with increasing amplitude of oscillation. The Payne effect increases with increasing concentration of filler material in the composite [33, 34].

The most important single parameter influencing the composite behavior is the average particle size of the filler. Structure reinforcement is readily obtained with sizes smaller than 100 nm but the particle geometry appears to be a more decisive factor in the mechanical behavior of the composite. Particle wetting and distribution are also important factors. Particles should be homogeneously distributed, as the loose agglomerates are potential failure initiation sites. Good wetting of particles by polymer chains is needed for forming a continuous composite structure; this can be a problem with metallic particles [33].

3.2 Models for predicting the mechanical properties of composites

The mechanical properties of MREs can be divided into two distinctive regimes: the composite properties (with different filler fractions) without applied magnetic field and the composite properties with applied magnetic field.

Different models have been developed for predicting the mechanical properties of polymer composite materials. The approximated shear modulus G_{ran} of elastomer filled with randomly distributed, spherical rigid particles is simply given by the equation:

$$G_{ran} = G_0 \left(1 + 2.5\Phi + 14.1\Phi^2 \right)$$

(3)

where G_0 is the shear modulus of the unfilled elastomer and ϕ is the volume fraction of filler particles [4, 8, 32]. This equation describes the behavior of a composite with an open, cubical arrangement of spherical particles, which are not closely packed. If the composite is stretched, the suspended particles perturb the stresses and strains, which are set up in the matrix. The equation is based on the hydrodynamic theory and the viscosity law presented by Einstein; the

perturbation by the particles leads to an increase in the dissipated energy and in the elastic energy. The term 2.5ϕ derives from the independent action of the filler particles and the term $14.1\phi^2$ from the mutual interaction of pairs of filler particles [8, 32]. The equation does not take into account the interaction of multiple particles.

Equation (3) can be further modified by replacing the filler volume fraction by the effective volume fraction (ϕ_{eff}), as most filler particles are non-spherical and can be agglomerated in complex structures [8]. The volume fraction ϕ_{eff} accounts for elastomer occluded inside the geometrically complex fillers. For the modified equation the basic assumption is that the matrix wets the filler particle surface but does not chemically react with it. However, the modulus of the composite depends on both the hydrodynamic effect and on the polymer-filler and filler-filler interactions, especially in the case of reinforcing fillers. Surface treatment of fillers can improve the compatibility between the filler particles and polymer matrix. The improvement in the reinforcing capability of the surface-treated fillers cannot be fully explained by Equation (3). In order to account for the increment in modulus due to various factors including the chemical interaction of the surface- treated fillers and the matrix, Equation (4) is proposed [8]:

$$\frac{E}{E_0} = a_m \, e^{\, b_m \phi} \tag{4}$$

where a_m and b_m are material constants at a particular level of strain and at a definite temperature. E/E_0 values measured at different filler contents have been fitted to Equation (4) at different strain levels. In this way a set of values for parameters a_m and b_m are obtained. Of these parameters, a_m is found to be independent on the strain level. The parameter b_m is dependent on the strain, which could explain the observed improvement in the polymer-filler interaction due to the surface treatment of the fillers [8].

Christensen [19] has developed general models for the elasticity of heterogeneous isotropic composite materials. In the determination of the effective stiffness properties (average stiffness of the composite) the properties and interaction of all the phases of the heterogeneous media are taken into account. The three-phase model considers rigid spherical inclusions embedded

in a continuous matrix. The third phase is the immediate surroundings of the inclusion, which has properties different from the matrix and the filler. The effective shear modulus is determined by equating the strain energy stored in the suspension of all three phases and in the equivalent homogenous medium. The suspension can be either dilute or non-dilute. In the dilute case, the inclusions are very small and so far away from each other that all interaction between the inclusions can be neglected. In the nondilute case, inclusions are large enough or there are so many of them that they can interact with each other [19].

Christensen has also developed a model for a concentrated suspension, where it is necessary to specify the packing arrangement of the inclusions [19]. The packing arrangement in the concentrated suspension model is assumed to be cubical. In the case of aligned MREs, the chain-like structure is often described as a cubical packing of rigid spherical particles [4, 25]. The shear modulus predicted by the concentrated suspension model depends only on the volume fraction ϕ of the rigid particles and on the shear modulus G_0 of the matrix. The following equation can be derived from the geometrical arrangement of the particles:

$$\frac{G}{G_0} = \frac{3\pi}{16\left[1-\left(\frac{\Phi}{\Phi_{max}}\right)^{1/3}\right]} \tag{5}$$

It must be emphasized that this model is only valid up to the maximum volume fraction for cubical packing, which is $\phi_{max} = \pi/6$. At volume fractions near the maximum value, the spherical particles are nearly in contact. In this condition most of the deformation occurs in those regions where the spheres are nearly in contact [4, 19].

3.3 Models for the field-responsive behavior of MR elastomers

Filling an elastomeric material with magnetizable particles influences the mechanical properties of the composite when an external magnetic field is applied. The origin of the field dependence of these properties is the existence of field-induced dipole type magnetic forces between the separate particles. The

behavior of MR elastomers can be thought as a combination of matrix properties and the properties of magnetizable particle network inside the matrix. Due to the interaction of magnetic particles, these elastomers exhibit a field dependent modulus at low strains. A field- induced increase in shear modulus reaching up to 60% has been reported for applied magnetic field strength values of about 0.8 Tesla [3–7, 12, 13, 10, 26].

Some models have been developed for describing the elastic behavior of the MREs under external magnetic field [3, 4, 9, 10, 25–28, 30, 31]. Most models describing the MR behavior are based on the magnetic dipole interactions between two adjacent particles in the chain. These interparticle interactions are then averaged over the entire sample to yield a model of the bulk magnetorheological behavior. Still a common weakness in the modeling of MR materials is the lack of understanding how magnetic flux density distributes itself within the particle network. For a development of such an understanding the magnetic nonlinearities and the effects of particle saturation must be taken into account. This problem has been studied using finite element approaches and analytical approximations [3–5].

On the basis of the dipole model for particle energy interaction, Jolly *et al.* [3] have developed a point-dipole model, where the MR effect is studied as a function of particle magnetization. This model is based on the previous studies on MR fluids. According to the model, the ferrous particles are magnetized linearly and it is assumed that in MR materials the strength is quadratically related to particle magnetization. In addition, the theory is then augmented with an approximate model of the relationship between the particle magnetization and average composite flux density. This model takes into account the gradual saturation of the magnetically permeable particles as the applied field strength increases. In the point-dipole model the local field and the sphere magnetization are assumed to be uniform. The model is semi-empirical; therefore it has to be fitted to empirical data by adjusting a parameter k_m that accounts for unmodeled magnetic interactions [3].

The point-dipole model is basically quasi-static and one-dimensional and it concentrates on the magnetomechanical properties of parallel chains of magnetically permeable spherical particles. In particular, a magnetic field is applied parallel to the chains and the shear strength caused by interparticle

forces is modeled. It is assumed that these particle chains are then embedded within a viscoelastic material, and that the viscoelastic properties of the composite are the sum of the viscoelastic properties of the composite with no field applied and the elastic/plastic properties induced by interparticle forces [3].

As the model is quasi-static, the dynamic effects of the magnetic field as well as inertial and rate-dependent effects of the particles are ignored. The particles are assumed to be uniformly distributed, homogenous spheres that can be magnetically modeled as identically induced dipole moments. It is also assumed that the particles are aligned in perfect chains (albeit with gaps between particles), and that quasi-static shear strains and associated stresses are uniformly distributed over the length of each particle chain [3].

In the point-dipole model, it is stated that the stress-strain relationship is independent of the particle size. However, the length of the gap h between the particles in a chain can be seen as a very important parameter; the magnetic field- induced stress is inversely proportional to the third power of this gap length. The maximum possible field- induced change in composite stress and modulus occurs when the aligned particles become magnetically saturated, i.e. when $M_p = M_s$. The maximum field-induced stress increases quadratically with the saturation magnetization M_s of the particle material. Therefore it is useful to select filler materials with high saturation magnetization [3, 6, 37].

Particle polarization is quite impossible to measure directly and it is very difficult to calculate. The model by Jolly *et al.* [3] includes a theory developed on the basis that saturation begins in the particle's polar regions at very low applied field strength values and increases towards total particle saturation as the applied field strength increases. Average particle polarization is then calculated as a function of average composite flux density [3].

In reality, the magnetic interaction between adjacent particle chains and packing arrangements is more complex than that occurring in simple linear chains. For example columnar structures with more than two contact points per particle can form structures resembling cubic lattice (FCC or BCC) or i.e. cylindrical aggregates [3]. Therefore a factor $k_m \geq 1$ has been added to accommodate for the magnetic interaction between adjacent particle chains and different packing arrangements. Adjacent particle chains will touch each other when the gap h

between the particles is $\pi/6\phi$, which corresponds to the maximum filler content for cubical packing. The distance h decreases, when the particle volume fraction increases [3].

Another approach by Davis [4] is focused in modeling the magnetomechanical properties of MR elastomers both in zero magnetic field and at saturation. He used the finite element method to analyze the dependence of the effective shear storage modulus of a MRE on interparticle magnetic forces. The work is based on prior theoretical and finite element analysis of MR fluids. In this model iron particles are treated as rigid spherical shells in continuous matrix. The rubber matrix is described in terms of the principal extension ratios (λ_i), which are the ratios of the current length (deformed) to original (non-deformed) length in the principal directions. Incompressibility is assumed, so that for any deformation $\lambda_1\lambda_2\lambda_3 = 1$. The shear modulus G_{ran} of rubber filled with randomly dispersed, spherical rigid particles is given by Equation (3). In finite element analysis the stress as a function of strain is calculated for different particle volume fractions, assuming that the particles are arranged in a simple cubical structure with periodic symmetry in chain direction and that the matrix is homogenous [4, 8].

In the situation, where the maximum change in shear modulus ΔG is obtained all the particles are magnetically saturated with magnetization $\mathbf{M} = M_s\,e_z$. The e_z is the unit vector in the z direction, so that the magnetization aligns with the applied magnetic field everywhere. Thus each particle has a magnetic dipole moment

$$\bar{m} = \frac{4\pi}{3}R^3 M_s\,e_z \qquad\qquad (6)$$

where R is the particle radius. On the basis of the dipole-dipole interaction, the magnetic contribution to the shear modulus is $\Delta G = \Delta G_0\,\Omega$, where

$$\Delta G_0 = \Phi\frac{\mu_0 M_s^{\,2}}{8} \qquad\qquad (7)$$

and

$$\Omega = -\frac{8R^3}{N}\sum_{l=1}^{Np}\frac{z_i^2}{r_i^5}\left[1 - \frac{5\left(y_i^2 + z_i^2\right)}{r_i^2} + \frac{35y_i^2 z_i^2}{r_i^4}\right] \qquad (8)$$

with the sum being over the N_p pairs of dipoles separated by vector displacements r_i ; $N_p = N(N-1)/2$ where N is the number of dipoles or particles in the MRE. Considering Fe particles for which $\mu_0 M_s = 2$ Tesla, the $\Delta G_0 = 0.3979\phi$ (MPa) and for isolated single chains of periodically spaced dipoles with separation d_c

$$\Omega = 4.808\left(\frac{2R}{d_c}\right)^3 \qquad (9)$$

If the chains are touching each other ($d_c = 2R$), $\Delta G = 1.913\phi$ (MPa). This result combined with Equation (3) suggests that the maximum value of $\Delta G/G_0$ occurs at the volume fraction $\phi = 1/\sqrt{14.1} = 0.266$ [4].

According to the finite element calculation by Davis [4], the stress is considerably higher for the elastomer containing a volume fraction of particles ϕ = 0.27. On the basis of this analysis, increasing the filler fraction over 27 vol.% does not further increase the absolute magnetorheological effect. This can be seen in Fig. 3, where the change of shear modulus ΔG divided by the zero-field modulus G(0) of the MRE is plotted versus the volume fraction of iron. It is also stated that with the same filler volume fraction when the gap h between the particles diminishes, the stress increases only slightly. This result predicts that the chaining of the particles does not influence the zero-field shear modulus of the composite. On the basis of the model the shear modulus of the aligned particle structure is not larger than $G(0)$ of the randomly distributed structure [4].
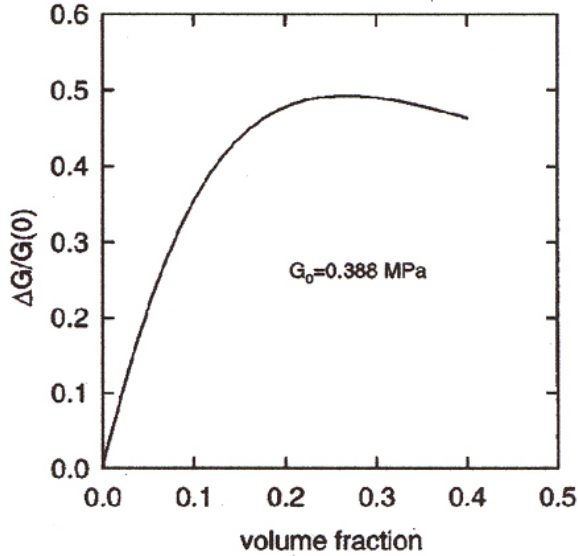
Figure 3. The predicted ratio of the change in modulus ΔG due to a strong magnetic field (B > 1 Tesla), where particle magnetization is saturated, to the zero-field modulus G(0) as a function of the volume fraction ϕ of particles. The unfilled elastomer shear modulus G_0 is 0.388 MPa [4].

Calculations using finite element analysis show that for typical MR elastomers the increase in the shear modulus due to the interparticle forces at saturation is about 50% of the zero-field modulus. However, the interaction among multiple chains, the clustering of chains, incomplete or imperfect formation of chains, etc. will influence this value. Calculations of the zero-field shear modulus perpendicular to the chain axis indicate that it does not exceed the modulus of a filled elastomer with randomly dispersed particles of the same concentration. This implies that the chaining of particles does not reduce the sensitivity or the relative response to magnetic field $ΔG/G_0$ [4]. The ratio $ΔG/G_0$ can be even higher than 0.5, if an elastomer with initially smaller shear modulus is used. Zhou [10] has reported that the maximum value for the ratio $ΔG/G_0$ is 0.6, when a soft silicone is used as a matrix.

In his model of aligned MREs, Zhou [10] has also taken into account the local saturation of particles and the influence of the deformation induced by the magnetic field on the constitutive equations of the matrix. As a deviation from the point-dipole model, his experimental studies using the free-vibration

technique have shown that the increment in shear storage modulus is linearly related to the applied magnetic field strength until magnetic saturation is reached. In addition to the point-dipole model, the subquadratic field dependence arising from the magnetic saturation of the poles of closely spaced pairs of particles occurs even when the applied field is well below the saturation magnetization. This approach yields a field-dependent modulus proportional to the applied magnetic field strength. The validity of the model ranges from small to moderate field strength values [10].

4. Elastic properties and vibration damping of MREs

Many materials, especially polymers show viscoelastic behavior. Viscoelasticity can be either linear or nonlinear. MR fluids behave as a linear viscoelastic body for sufficiently small strain amplitudes (pre-yield regime), while nonlinear viscoelastic behavior is observed at high strain amplitudes (post-yield regime). Under oscillatory shear, MR fluids show elasticity-dominated properties in the magnetic field. Both the storage modulus and the loss modulus increase significantly with increasing field strength. [15].

MR elastomers are normally operated in pre-yield regime in the linear viscoelastic region with small deformation. The MREs are intended to be used as structural materials in applications, where the load is often of a dynamic type. The proposed application of MREs is to adjust the natural frequency, which is controlled by the equivalent stiffness of the structure [10]. The dynamic elastic properties of MREs can be studied using different methods. Mechanical methods for measuring dynamic elastic properties can be divided into three types: quasi-static, resonance and time-of-flight. The quasi-static methods, such as cyclic loading, do subject the samples to relatively slow deformations (0 to 1000 Hz). Resonance techniques measure the frequencies of the elastic resonances of free or forced oscillations of the specimen and the time-of-flight methods measure the transit time of an elastic wave across the specimen. The latter two can also be used at very high frequencies [23].

In cyclic dynamic loading, the material deforms and returns back to its original form during one cycle. The oscillating force is varied periodically, usually with a sinusoidal alteration at the angular frequency ω. A periodic experiment at frequency ω is qualitatively equivalent to a transient experiment during cycle time $t = 1 / \omega$ [18].

The MREs belong to the group of viscoelastic materials. When they are subjected to sinusoidally oscillating stress, the strain is neither exactly in phase with the stress nor totally out of phase. Usually it is somewhere in between. If the viscoelastic behavior is linear, the strain and the strain rate are infinitesimal and the time-dependent stress-strain relations can be described by linear differential

equations. The strain will alternate sinusoidally but out of phase with the stress. The amplitude of the stress $\sigma_0(\omega)$ can be expressed in sinusoidal form [18]:

$$\sigma = \sigma_0 \sin(\omega t + \delta) = \sigma_0 \cos\delta \sin\omega t + \sigma_0 \sin\delta \cos\omega t \tag{10}$$

where σ_0 is the maximum amplitude of the stress, ω is the angular frequency, t is cycle time and δ is the phase angle or mechanical loss angle, whose range is between $0° < \delta < 90°$. In viscoelastic materials, some of the deformation energy input is stored and recovered during each cycle and some is dissipated as heat. The storage (or in-phase) modulus, G', represents the ability of the viscoelastic material to store the energy of deformation, which contributes to the material stiffness. The loss modulus (or out-of-phase) G'' represents the ability of the material to dissipate the energy of deformation. They can be defined as a function of the angular frequency [18]:

$$\sigma = \gamma_0 (G' \sin\omega t + G'' \cos\omega t) \tag{11}$$

where γ_0 is the maximum amplitude of strain. It is usually convenient to express the sinusoidally varying stress as a complex quantity. Then the dependence of the in-phase stress and out-of-phase stress on the strain of the viscoelastic material can be presented using the complex modulus G^* [18]:

$$G^* = G' + iG'' \tag{12}$$

Another term widely used for deformation studies of viscoelastic materials is the ratio between the loss and storage moduli:

$$\tan\delta = \frac{G''}{G'} \tag{13}$$

where $\tan\delta$ is called the loss angle or loss factor. In vibration damping, $\tan\delta$ and G'' can be used for describing the efficiency of damping caused by the material [15, 18].

The silicone elastomers have been used extensively as the matrix materials for magnetorheological elastomers. The activation energy of the silicones for viscous flow is very low and the viscosity is less dependent on temperature than the viscosity of hydrocarbon polymers. The cross-linked three-dimensional structure consisting of helical spring-like formations allows viscoelastic movement in all three dimensions and has a high degree of elastic restoration capacity, as shown in Fig. 4 for a polydimethylsiloxane (PDMS) silicone [17].

$$CH_3 - Si - O - (Si - O)_3 - Si - CH_3$$
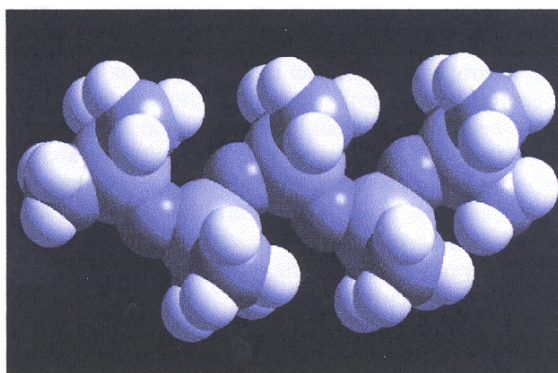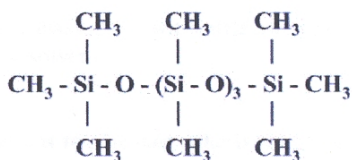
Figure 4. Helical structure of the polydimethylsiloxane backbone [17].

For most solids the bulk modulus K and shear modulus G are of the same order of magnitude. Elastomers at temperatures above the glass transition consist of cross-linked, tangled polymers with high segment mobility. Under twist or tension the segments readily realign themselves in the direction of the applied force. The elastomers are densely packed, and as such they are not particularly compressible. Although the shear modulus of an elastomer generally very low (in the MPa range) the bulk modulus of elastomers is comparable to that of

elastic solids (in the GPa range). The temperature has a marked influence on the shear modulus, but a much smaller effect on the bulk modulus. The Poisson's ratio ν is typically high, for silicone elastomers it is very close to 0.5 [18, 23].

The filler materials influence the overall properties of the elastomers also without external magnetic field. This influence increases, when the volume fraction of the filler material increases. Lokander *et al.* [7] have shown that the absolute MR effect of isotropic MREs (the difference between the zero-field modulus and the modulus measured under external field) is quite independent on the matrix material. However, the zero-field modulus can be much larger for a harder matrix material, which means that softer matrix materials may show a greater relative MR effect. Materials with high volume fraction of rigid filler material have already high zero-field modulus, so that the relative MR effect can be quite low [7]. In addition, tensile tests by Lokander *et al.* [6] show that increasing the filler fraction over 30 vol.% will deteriorate the mechanical properties of the elastomer composite [6].

The viscoelastic properties of the MREs depend on the orientation of the particles, but it is still not very clear how the filler alignment influences the elastic properties of the composite. The properties of aligned MREs with multiple contact points between the particles have been compared to materials with cubic crystal lattice [3, 4, 25]. Davis [4] has stated that the zero-field shear modulus of aligned MREs is not larger than the modulus of similar material with a random distribution of rigid particles. Bellan and Bossis [9] have characterized homogeneous and aligned MREs in dynamic tensile testing. They have noted that in the absence of an external magnetic field the Young's modulus is much higher for the aligned material in the chain direction than for the homogeneous material with the same filler volume fraction.

Homogeneous MREs with a random distribution of particles can be considered as isotropic materials. A solid, which is isotropic in its elastic constants, is a material where the elastic moduli are not dependent on directions. Few studies have addressed the properties of isotropic MREs and only three of them [9, 14, 30] compare the mechanical properties of isotropic and aligned MREs [6, 7, 9, 14, 25, 30]. The relation between the stress and strain of solid materials is the well-known Hooke's law, where c_{ij} is the elastic stiffness tensor [21]:

$$\sigma_i = \sum_{j=1}^{6} c_{ij}\, \varepsilon_j \tag{14}$$

For a three-dimensional object, an off-axis surface stress produces nine stress components (3 normal, 6 shear). The corresponding equations of c_{ij} comprise a 9×9 matrix which can be reduced through a subscript translation to a 6×6 matrix. The symmetry properties of crystals still reduce the number of independent elastic constants. Imposing only the minimum symmetry of the cubic system reduces the number of independent elastic constants to 3, and this number is further reduced to 2 for an isotropic material. The elastic stiffness constant matrix for isotropic materials is [21]:

$$c_{ij} = \begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ & c_{11} & c_{12} & 0 & 0 & 0 \\ & & c_{11} & 0 & 0 & 0 \\ & & & \frac{1}{2}(c_{11} - c_{12}) & 0 & 0 \\ & & & & \frac{1}{2}(c_{11} - c_{12}) & 0 \\ & & & & & \frac{1}{2}(c_{11} - c_{12}) \end{bmatrix} \tag{15}$$

All the important elastic constants for an isotropic solid are expressible in terms of the two above-mentioned constants: the Lamé constant λ and shear modulus G. For example, the longitudinal modulus c_{11} is defined by

$$c_{11} = \lambda + 2G \tag{16}$$

and the shear modulus G is

$$G = \frac{1}{2}(c_{11} - c_{12}) \tag{17}$$

In a cubical system, three independent elastic constants are needed to describe the elastic properties. These are c_{11}, c_{12} and the shear constant c_{44}.

4.1 Influence of external magnetic field on the elastic properties of MREs

Borcea and Bruno [25] have developed a comprehensive model for the behavior of isotropic MREs in the external magnetic field with fully coupled magneto-elastic interactions. The distribution of the magnetization in the composite material is calculated from the basic minimum energy principle of magneto-elasticity. This model considers only isotropic MREs. Dorfmann and Ogden [31] have also summarized a system of constitutive equations for an isotropic magneto-sensitive Cauchy-elastic solid within the framework of the electromechanical and thermo-mechanical theories. They have shown theoretically, that the existence of a magnetic field makes the shear response of an isotropic MRE stiffer.

Farshad and Benine [39] have characterized isotropic and aligned MREs in tension and in compression. The aligned MREs were oriented either longitudinally or transversely to the applied load. They found that the alignment direction influences the tensile properties of the MRE. Samples aligned longitudinally to the tensile load direction exhibited the highest tensile strength. In static compression, the applied magnetic field increased the stiffness of both isotropic and aligned MREs.

Shiga *et al.* [26] have analyzed the modulus change of aligned MREs by simplifying the dipole interactions in the direction of the external field. Their model takes into account only the magnetic interaction between the two nearby dipoles. The results suggest that in aligned MREs the increasing shear modulus is quadratically dependent on the magnetic field strength.

Shen *et al.* [27] have developed a model, which takes into account the dipole interactions in a particle chain and the nonlinear properties of the host composite. The increase of the shear modulus ΔG induced by an external magnetic field depends on the number of particle chains in a unit cross section. The increase of the shear modulus under the influence of a magnetic field is quadratically proportional to the value of the dipole moment, which in turn depends on the ratio of the mean distance between two adjacent particles over the mean radius of the particles. In order to obtain a large change in modulus, the particle volume fraction should be relatively high. Bellan and Bossis [9] have also considered aligned MREs as analogous to the fiber-reinforced composites.

In MREs, the fibers consist of particle chains, whose stiffness is very sensitive to the amount of polymer in the gaps between the particles. The stiffness of the "fibers" formed by particles is increased by the application of magnetic field and the stiffness of the composite depends on the number of chains per unit cross section.

According to Yalcintas and Dai [28], the external magnetic field will influence the strain amplitude, loss factor and the natural frequency of the vibrating MRE system in dynamic testing in the pre-yield regime. They have studied both theoretically and experimentally the vibration behavior of a sandwich beam structure consisting of a MRE material between two elastic Al layers. Results from both studies show that when the magnetic field strength increases, the strain amplitude decreases and natural frequencies shift to higher values. The loss factor (tan δ) values were found to increase with magnetic field strength in all vibration modes, although Yalcintas and Dai predicted theoretically that the loss factor should decrease in the first mode and then increase in higher modes. The different models quite profoundly explain the field-induced increase of the shear storage modulus. However, there is no complete explanation for the variations of the loss factor with magnetic field [28].

When applying an external magnetic field but no mechanical loads, the MREs will slightly deform. Borcea and Bruno [25] showed theoretically that an isotropic MRE would expand in the direction of the applied magnetic field while an aligned MRE will compress, if the applied field is parallel to the oriented structure. Zhou and Jiang [30] have proved this experimentally; they also stated that the deformations are related to the applied field strength. The magnetically induced deformation of an aligned MRE in the chain direction changes only slightly with different filler volume fractions. The deformation of an aligned MRE driven by external magnetic field is smaller than that of isotropic MRE with the same volume fraction. This means that in the chain direction aligned MREs are stiffer than isotropic MREs [30].

4.2 Influence of external magnetic field on vibration damping in MREs

Damping is a process, which dissipates energy in a vibrating system. Damping forces resisting the vibrations may arise from several sources, such as air or fluid

resistance, electrical damping, internal friction due to material phases with different elasticity or from external friction. Simple damping processes such as viscous, structural and Coulomb damping have been used for describing the energy loss mechanisms in dynamic systems. Viscous damping occurs when the damping force is proportional to the vibrational velocity of the system. On the contrary, in the Coulomb or dry frictional damping the friction force is independent on velocity. Structural damping describes the anelasticity of the system and consequent internal friction. In structural systems it is often convenient to combine various damping forces into one factor. The various types of damping can be replaced for instance by equivalent viscous damping. The equivalent damping is determined so that it produces the same dissipation of energy per cycle as the dissipation produced by the actual forces. For example, the damping produced by internal friction can be described by equivalent viscous damping [20].

In the case of MREs, the basic material damping can be considered to be of viscous character. Subjecting the system to forced oscillations or studying the free vibration response of the system the vibration damping can be studied if the damping is on a subcritical level. The critical level of damping is defined as the smallest amount of damping for which no oscillation occurs in free vibration response of the system to an external impulse. In practical cases damping is usually smaller than the critical value. The viscous damping constant b describes the damping rate of the material and it has dimensions of force per unit velocity. It can be obtained from the dynamic equilibrium equation of viscoelastic motion for a single degree of freedom (SDOF) system:

$$m\,\ddot{z}\left(t\right)+b\,\dot{z}\left(t\right)+k\,z=F_0\,e^{\,i\omega t} \tag{18}$$

where F_0 is the external oscillating force, m the effective mass, z the displacement amplitude and k the spring constant of the system. However, as the value of the viscous damping constant depends on the dimensions of the specimen, the dimensionless damping ratio ξ of actual damping to the critical damping value is often used instead of b. The critical viscous damping constant is defined as $b_c = 2m\omega_0$, where m is the effective mass of the vibrating system and ω_0 is the natural frequency. The damping ratio ξ is defined as [20]

$$\xi = \frac{b}{b_c} = \frac{b}{2\,m\,\omega_0} \tag{19}$$

Eq. (18) is the dynamic equation of motion, where the steady-state response of the system F_0/k is multiplied by a dynamic magnification factor, which in turn is a function of the frequency ratio β and the damping ratio ξ. The frequency ratio β is the ratio of the angular frequency to the natural frequency of the system $\beta = \omega/\omega_0$ [20, 24]. By using this dynamic magnification factor Eq. (18) can be written in the form:

$$z = \frac{F_0}{k}\sqrt{\left[\left(1 - \beta^2\right)^2 + \left(2\,\xi\,\beta\right)^2\right]} \tag{20}$$

where the square root term represents the dynamic magnification factor. For describing the damping of a vibrating system, the damping or the loss factor η (tan δ) of the system is often used. It is defined as the ratio of dissipated energy to the energy stored by the system. The loss factor is equal to the ratio of the imaginary part of the complex modulus to the real part of the modulus as described in Eq. (13) [18].

The damping has only a minor influence on the response of the system in the frequency regions either well below or well above the resonance frequency, but it is of great importance near the resonance condition. In the range of $\omega \ll \omega_0$, where the vibration is almost the same as produced by the static action of the force, or in the range of $\omega \gg \omega_0$, where the high-frequency disturbing force produces practically no forced vibrations of the system, damping has only a secondary effect on the value of the magnification factor. In these regions, the damping effect can usually be neglected. In the case of forced vibrations, the most important damping occurs at or near the resonance. Near the resonance condition the magnification factor grows rapidly and it is very sensitive to the changes in damping. Damping near the resonance situation cannot be disregarded in order to obtain meaningful results [20].

MR fluids are used in engineering to produce a damping effect. MR fluids can be used for changing the damping ratio of the structures since they operate within the post-yield regime. MR elastomers, however, operate within the pre-

yield regime and they are characterized by their field-dependent modulus. Due to the ability to change modulus with the field, MRE materials can be used in structures to adjust the natural frequency, which is dependent on the equivalent stiffness of the structure. With increasing shear modulus, the natural frequency shifts to higher frequencies. By adjusting the natural frequency, one can prevent the system from attaining the resonance or other coupled phenomena [10, 13].

The natural frequency of the MRE is dependent on the applied magnetic field. Zhou [10] has shown that when the magnetic field strength increases, the natural frequency of the system increases with the field strength until the magnetic saturation of the composite occurs. This saturation is seen to occur at about B_{MRE} = 0.8 Tesla for iron filler. This phenomenon suggests that the natural frequency is influenced by the magnetic force between the filler particles inside the material. When the saturation occurs, the magnetization of each particle will remain constant and the magnetic force between the particles does not change much with the applied field. Therefore, the natural frequency does not change with the applied field within such a regime [10]. The increase of the natural frequencies of MRE in magnetic field is also found by Ginder *et al.* [5] and Yalcintas and Dai [28].

It is suggested that in addition to the increase in shear modulus, an increase in vibration damping is also occurring due to the applied magnetic field in the MREs. However, the vibration damping properties of the MREs have not been studied as widely as the changes in the field-dependent storage modulus. Different opinions exist whether or not the application of a magnetic field increases vibration damping capacity in the MREs. Lokander *et al.* [7] have measured the damping factor (tan δ) for a nitrile rubber (Perbunan 3445) with an iron content of about 37.8 vol.% with and without the magnetic field. They have found that in these isotropic MR elastomers there is a small increase of about 0.01–0.02 in loss factor as a result of a large applied magnetic field (0.8 Tesla) in the frequency range of 1–20 Hz (Fig. 5). Jolly *et al.* [3] have also noted an increase of 0.03 in tan δ values at higher peak strains (10%) in shear testing of aligned MR elastomers containing 30 vol.% of iron. The measurements were done at 10 Hz with a magnetic field strength of 0.85 Tesla. A substantial drop in modulus accompanied this increase. However, the measured increase in tan δ was too small to be of any practical importance [3, 7].
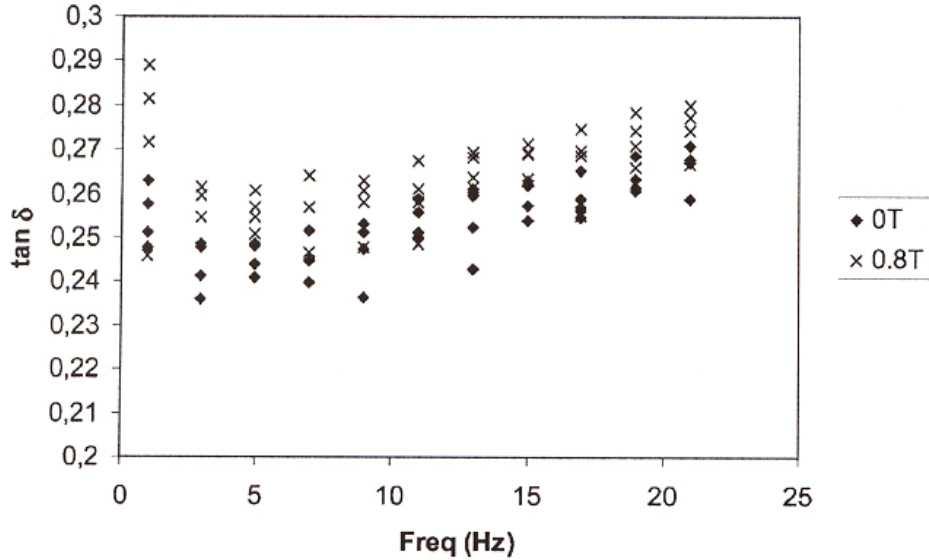
Figure 5. Loss factor (tan δ) of an isotropic MRE with 37.8 vol.% of iron as a function of the frequency, when measured without magnetic field and with applied magnetic field strength of approximately 0.8 Tesla [7].

Zhou [10] has measured the damping ratio ξ as a function of magnetic induction in a vibrating system consisting of an aligned silicone MRE with 27 vol.% of Fe (Fig. 6). The damping ratio ξ of this system was measured to be 0.24 in zero field. With increasing magnetic field strength, the damping ratio decreased slightly (by less than 10%). According to this study, the damping ratio of a MRE is relatively independent on the magnetic field strength and the ratio of the energy dissipated by the damping mechanism of the MRE to the total elastic deformation energy is not influenced by the magnetic field [10, 12]. A decrease of the measured loss factor in magnetic field is also found in reference [14].
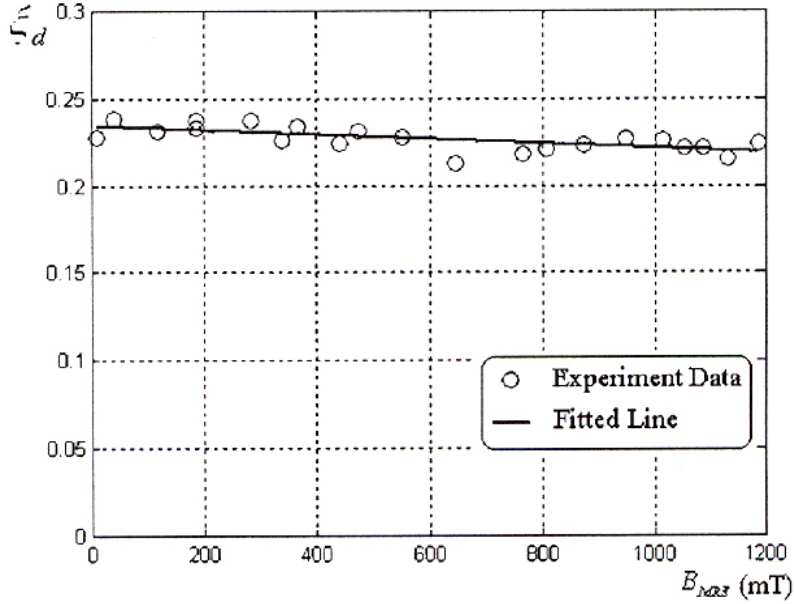
Figure 6. Damping ratio ξ_d of the vibration system consisting of aligned silicone MRE with 27 vol.% of Fe as a function of the magnetic induction B_{MRE} [10].

Ginder *et al.* [13] have measured the loss factor (tan δ) value of 0.22 at zero field for an aligned natural rubber MRE with 27 vol.% of carbonyl iron. The MRE was connected to a tuneable vibration absorber. The loss factor value was found to be decreasing slightly with increasing field strength. In reference [40], the measured increase in both the shear modulus and loss factor was 30% from the zero-field values for the similar kind of material, when the field strength was increased from 0 to 1.2 Tesla. In this study, the MRE was characterized in double-lap shear, with shear stresses applied in a plane perpendicular to the direction of chain alignment. In reference [41], Ginder *et al.* have measured the stiffness and damping capacity of a prototype automotive bushing made of the same MRE. The stiffness and damping increased approximately linearly with applied coil current and they were 25% larger than their zero-field values when the field strength was near 1.8 Tesla.

Bellan and Bossis [9] have measured in dynamic tensile testing a value of 0.16 for a zero-field tan δ and the value of 0.22 with applied magnetic field strength of 0.53 Tesla for an aligned silicone MRE with 30 vol.% of Fe, which also indicates that the damping is increased in magnetic field. Yalcintas and Dai [28]

have obtained similar results. They found that in forced oscillation the loss factors measured for all modes of vibration of a beam consisting of a MRE layer between Al plates were increased in magnetic field. Their results are presented in Fig. 7.
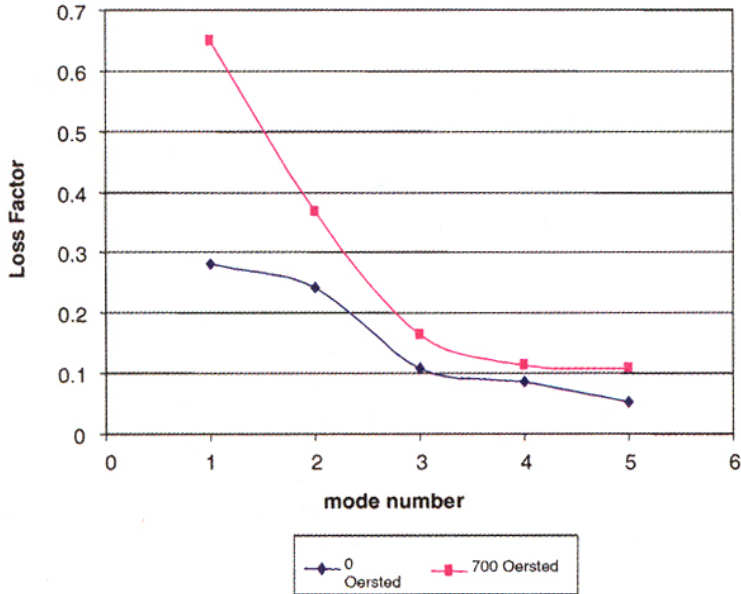

Figure 7. The loss factor values of different vibration modes measured for the sandwich beam structure consisting of an aligned MRE layer with 30 vol.% of iron in between Al sheets, as measured in zero-field and with applied magnetic field strength of 700 Oe (0.7 Tesla) [28].

4.3 Dynamic mechanical testing of MR elastomers

In various studies dynamic mechanical testing has been used for characterizing the shear storage modulus of aligned MR elastomers. In many of these studies a sandwich structure has been used, where the MR elastomer layer is adhesively bonded between two or three (double lap shear) metallic plates. Most of the testing has been carried out by using forced oscillations. Only recently the free-vibration techniques have also been used in MRE studies. In almost all of the studies, the applied magnetic field direction has been parallel to the aligned particle structure in order to maximize the interaction between the particles in

chains. A field-induced increase of up to 60% in shear storage modulus has been reported at saturation magnetization of the filler particles [3, 6, 10].

The MR effect in MR elastomers is described as a reversible change in modulus in applied magnetic field. This has been confirmed in several studies [1–14, 25–28, 30, 31]. Aligned MREs have been characterized mostly at relatively low frequencies (1 to 20 Hz) to measure the changes in the dynamic shear storage modulus induced by the external magnetic field [1, 3, 5–8, 10, 13]. Ginder *et al.* [5, 13] have used a tuned vibration absorber (TVA) in resonance to study the dynamic shear modulus of MR elastomers containing 27 vol.% of Fe in the frequency range from 100 to 1400 Hz. They found a substantial MR effect over the entire frequency range studied. The increase in the shear modulus initially varied quadratically with magnetic field strength but saturated at higher field strength values. When the strength of the magnetic field was increased from 0 to 0.56 Tesla, the consequent increase in shear modulus was nearly 2 MPa and the resonance was shifted upward in frequency by over 20%. Zhou *et al.* [10, 12] have studied silicone MREs with 27 vol.% of Fe in damped free vibration. Their experimental results reveal that the field-dependent behavior of aligned MREs is related to the applied frequency.

In addition to the testing frequency, the MR effect depends on the applied strain amplitude. This is due to the fact that the magnetic forces depend strongly on the distance between the dipole particles [5, 7]. The onset of particle chain yielding in aligned MREs has been observed in the vicinity of 1–2% strain and the MR effect is decreasing gradually with increasing amplitude [26]. The dynamic stiffness without the applied field decreases when the strain amplitude increases, which is typical to filled elastomers [3, 26, 33, 34]. The maximum MR effect can be obtained at relatively small strain amplitudes when the interaction between the particles is at strongest. Generally, when the particle chains subjected to external load start to yield, the MR effect diminishes [7, 9, 26]. The strain-dependent behavior of the shear modulus is related to the opening of the network structure of aggregates when the strain increases; this is known as the Payne effect in vulcanized rubber. Similar behavior is also observed for the storage and loss modulus [5, 9, 33, 34].

Jolly *et al.* [3] have measured the properties of aligned MR elastomers by using double lap shear. The complex modulus of aligned samples has been measured

at various frequencies, strains and applied magnetic field strength values. The influence of average magnetic field strength on the elastic modulus is shown in Fig. 8 for three MRE specimens with 10, 20 and 30 vol.% of carbonyl iron. The change in modulus increases monotonically with increasing volume percentage of iron. While the maximum increase in modulus is nearly 0.6 MPa with the iron volume content of 30%, the maximum relative increase of the modulus in magnetic field remains relatively constant between 30–40% for the three samples (Table 2). A pronounced drop in the magnetorheological effect and a corresponding increase in the field dependent energy dissipation (tan δ) was noted at strains above 1–2%. This strain dependency was attributed to the onset of yielding of the particle chains. The yield strain is the maximum strain where the MR effect is still notable; at higher yield strains the MR effect diminishes. MR elastomers exhibit a yield strain several times higher than the analogous MR fluids [1, 3, 7].
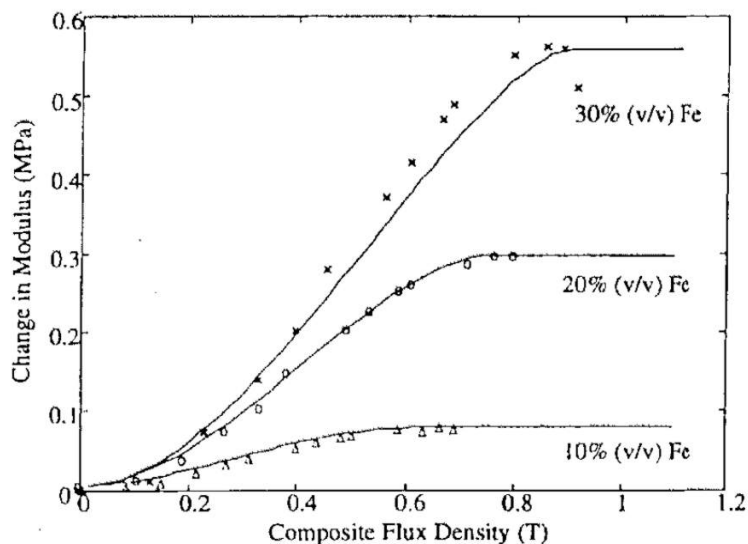

Figure 8. Influence of the average magnetic flux density (magnetic induction) in the composite on the elastic modulus for MR elastomers containing 10%, 20% and 30% of carbonyl iron by volume [1].

Table 2. The nominal modulus (no field applied) and the experimentally measured maximum change in modulus for MRE specimens containing 10, 20 and 30 vol% of carbonyl iron as measured at 1.0% strain and at 2.0 Hz. The maximum change in the modulus as predicted by the model of Jolly et al. [3] (assuming no gaps between particles) is also shown in the table.

Filler content in the test specimen:	*Nominal modulus (MPa):*	*Max. change in modulus, experimental (MPa):*	*Max. change in modulus, model (MPa):*
30 vol.% Fe	1.80	0.56 (31%)	0.55
20 vol.% Fe	0.74	0.29 (39%)	0.36
10 vol.% Fe	0.26	0.08 (30%)	0.17

The response of MR elastomers to shear deformation can also be studied by using an oscillatory rheometer with an inductance coil surrounding the composite sample. Sample oscillation in a DC magnetic field produces an e.m.f. due to the shear-induced magnetization, which is measured by a lock-in amplifier. The e.m.f produced in oscillation is linearly dependent on the oscillation frequency ω, quadratically dependent on the strain amplitude and proportional to the shear modulus [11].

Zhou [12, 45] has studied the vibration of a system consisting of an aligned MRE with 27 vol.% of Fe with a non-magnetic weight under displacement excitation in free vibration. He has found that the field-dependent behavior of aligned MRE is related to the applied frequency. In the low frequency regime the mechanical properties of the MRE change slightly with the applied magnetic field. In the moderate frequency regime, the field-dependent properties of the MRE appear and they are highly nonlinear. In the high frequency range, the field-dependent properties are different from those of the moderate frequency range. The area of the hysteresis loops in the two measured acceleration domains decreases with the applied magnetic field [12, 45].

Bellan and Bossis [9] have characterized isotropic and aligned MR elastomers in static and dynamic tensile testing. They have found that in the absence of an external field the Young's modulus is much higher for the aligned material than for the isotropic one. This effect is due to the presence of a chain-like particle structure. The stiffness of the chains is very sensitive to the amount of polymer in the gap between the particles. The stiffness of the chains can be reinforced by the application of an external magnetic field and hence by introducing magnetic attractive forces between the particles [9].

Bellan and Bossis [9] have divided the increase of stress $\Delta\sigma$ of aligned MREs in the magnetic field in two parts: the initial stress $\Delta\sigma_i$ occurs at very low strain (10^{-4}) and the remaining part $\Delta\sigma_{st}$ depends of the strain. They have noted that in tensile testing the initial stress $\Delta\sigma_i$ increases with the magnetic field and that the maximum stress shifts towards higher strains when field strength is increased. This can be explained by a model proposed by Cox (1952), which is based on the calculation of local stresses around a cylindrical fiber inside a composite. This model considers solid fibers of certain length L placed in the matrix. As long as the matrix is attached to the fiber, the average strain and the average stress in the matrix around the fiber grow linearly with the length of the fiber. The integration of this stress along the fiber shows that the mechanical stress σ^L_f in the center of the fiber will grow proportional to the factor $L^2\varepsilon$. On the other hand, the magnetic stress σ_H ($\sigma_H \propto H^2$) prevents the fiber from breaking as long as the mechanical stress in the fiber center is lower than the magnetic stress. The breakdown will occur when the mechanical stress becomes larger than the magnetic one [9].

According to this model the initial stress $\Delta\sigma_i$ is related to the existence of long chains, which will break at such a low strain that it seems that the stress is acting without strain. When increasing the strain, these "fibers" will break again keeping the average stress at a constant level. If there are also short fibers present in the matrix, they will give rise to an increase of stress up to the strain ε_{max} where they begin to break. Such a model with two typical (long and short) lengths of chains explains the initial stress and the presence of maximum stress; the decrease of the stress at higher strains is due to the progressive separation of the particles [9].

Lokander *et al.* [6, 7] have studied the dynamic shear modulus for isotropic MR elastomers with different filler particles and matrix materials. The modulus was measured at frequencies of 2, 10 and 50 Hz and with strain amplitudes of 1.1, 2.8, 5.4 and 11% with and without a magnetic field. They measured the MR effect as a function of strain amplitude and found that the MR effect decreases rapidly with increasing applied strain within the measured strain range, but that it is independent on the testing frequency. The highest absolute MR effect on composite shear modulus was about 0.8 MPa for nitrile rubber (Perbunan 3445) with about 32 vol.% of iron, when measured at 5.4% strain and in magnetic field of about 0.8 Tesla. The fact that the absolute MR effect is independent on the matrix material means that softer matrix materials will show a greater relative MR effect. The zero-field modulus can be decreased and the relative MR effect can thus be increased by the addition of the plasticizers to the matrix or by using a soft matrix material, such as silicone elastomer [7, 10].

5. Preparation and process variables of MRE composites

MR elastomers consist of magnetically permeable particles in a non-magnetic elastomer matrix. Several kinds of polymers and elastomers have been used as matrix materials. In addition to the actual polymer, additives like crosslinking agents, antioxidants and mixing aids may be used. As a filler material, carbonyl iron has been used in various studies due to its extensive use in MR fluids. Other kinds of pure iron have also been used. Some of the used filler materials are listed in Table 3 [5]. The behavior of MR elastomers without the external magnetic field depends basically on the characteristics of the composite material. When external magnetic field is applied, the cohesive forces between the magnetically polarized particles influence the viscoelastic properties of the MR elastomers. In the following chapters, the influence of some process variables on MRE properties is studied and discussed.

Table 3. Some filler materials used in MR elastomers.

Filler particle type:	*Composition and shape of the particles:*	*Particle size, average (μm):*	*Used in reference:*
ISP-3700	Carbonyl iron, spherical	3	5, 10, 13
ISP R-2521	Carbonyl iron, spherical	5	2
BASF SQ	Carbonyl iron, spherical	3.9–5.0	6
BASF EW	Carbonyl iron, spherical	3.5, 13, 23	14
BASF HQ	Carbonyl iron, spherical	2	9
Höganäs ASC100.29	Pure iron, irregular	< 180	6
Höganäs AT40.29	Pure iron, irregular	200	6
Höganäs ASC300	Pure iron, irregular	< 60	6

5.1 Influence of the matrix material on the MRE behavior

Many different elastomers and gels have been used as matrix materials in the MREs. These include, for example, natural and synthetic rubber, silicone elastomers, polyurethane and polyvinyl alcohol [3, 4, 5, 6, 7, 27]. The most important character of the matrix material, besides the rheological properties is that the magnetic permeability is as low as possible. If the matrix material is magnetic, the polarization of the particles will be less effective and the MR effect therefore smaller. The addition of magnetically active fillers (other than MR particles) will also decrease the MR effect [5, 6].

The filler materials influence the overall properties of the elastomer composite also without external field. This effect increases, when the volume fraction of the filler material increases. Lokander *et al.* [7] have shown that the absolute MR effect (the difference between the zero-field modulus and modulus measured under external magnetic field) is independent on the matrix material. However, the zero-field modulus can be much higher for hard matrix material, which means that softer matrix materials will show a greater relative MR effect. Materials with high volume fraction of iron have already high zero-field modulus, which means that the relative MR effect is quite low [6, 7].

5.2 Influence of particle size, shape and volume fraction on the behavior of MREs

In MR fluids the particle size varies typically from 0.1 to 10 μm. These values are from one to three orders of magnitude larger than those typical for colloidal ferrofluid particles. Larger particles allow for obtaining stable, highly magnetizable materials and reversible particle aggregation. Nanoscale particles agglomerate easily but cannot be separated again once they have agglomerated. Typical micron-sized MR filler particles will support hundreds of magnetic domains. The particles should be large enough to support at least several magnetic domains in order to have a substantial MR effect. In MR elastomers the particle size can be varied in a larger scale than in MR fluids, as the sedimentation is not a problem [1].

The model by Jolly *et al.* [3] suggests that the stress-strain relationship of the MREs is independent on the particle size. Lokander *et al.* [6, 7] have shown experimentally, that the particle size and shape have an influence on MR properties. They measured the magnetorheological effect for isotropic nitrile rubber MRE with varying iron particle size and content. The MR effect was larger for materials with ASC300 iron (particle size < 60 μm) than for materials with carbonyl iron (particle size 3.9–5.0 μm). For even larger particles than 60 μm, the measured MR effect appeared to be slightly smaller.

Demchuk and Kuzmin [14] have also studied the influence of filler particle size on the shear storage modulus and loss factor of isotropic and aligned MR elastomers. They have found that in the absence of the field the modulus for MRE with larger particles (13 μm) is smaller than for fine particles (3.5 μm). Under the action of the magnetic field the situation is reverse: as the field strength increases the modulus of the MRE with larger particles significantly exceeds the modulus of the MRE with fine particles. On the other hand, the measured loss factor decreases as either the magnetic field strength or the filler particle size increases.

The apparent density of metal powders is much smaller than the density of bulk metallic material. Loosely packed powder always contains air in between the particles. If the air is replaced by elastomer, the critical particle concentration (CPVC) is defined as the concentration, at which the particles are in touch with each other and the voids between them are completely filled with the elastomer. At concentrations higher than CPVC, there is not enough elastomer to fill all the voids between the particles and the mechanical properties of the composite will be poor. The stiffness of the material due to the increased filler content will also increase substantially and therefore the relative MR effect will not increase significantly. This also means that the relative MR effect will show a maximum around the CPVC. The CPVC value for different powders can be calculated from their apparent and bulk density [6].

$$CPVC = \frac{100 \times \rho_{app}}{\rho_{Fe}} \qquad (21)$$

The calculated CPVC values of different iron powders are presented in Table 4.

Table 4. The calculated CPVC values for MR elastomers with different iron fillers.

Filler particle type:	Apparent density (g/cm³):	Critical particle volume concentration (vol.%):	Reference:
ISP-3700	1.9 (1.5–3.0)	24.1	ISP (analysis)
BASF SQ	2.3	29.1	BASF (analysis)
Höganäs ASC300	2.88	36.5	6
Höganäs ASC100.29	2.98	37.7	6
Höganäs AT40.29	3.02	38.2	6

When the powder particle size is small, the tendency of forming agglomerates will grow. Therefore for carbonyl iron the CPVC can be higher than the calculated value, if the agglomerates can be destroyed and particles are well dispersed in the matrix. The agglomerates create local anisotropy in the material. The anisotropy may influence the MR properties in two ways: the local anisotropy may be beneficial if it is in the direction of the field, but it may lead to a decrease in the MR effect if it is perpendicular to the field [6].

The optimum particle volume fraction for the largest relative change in modulus at saturation is predicted to be 27% [4]. Shiga *et al.* [26] have measured the increase in shear modulus as a function of the particle volume fraction. For aligned MREs, the change in shear modulus is increasing with increasing particle volume fraction. At filler concentrations higher than 30 vol.%, the mechanical properties of the composite deteriorate rapidly and the stiffening of the material is larger than the increase of the MR effect. Lokander *et al.* [6, 7] have measured the tensile strength of isotropic MR elastomers. The measured fracture stress as a function of iron content was almost constant for iron contents up to approximately 30% by volume. At higher iron contents the measured fracture stress was much lower [6]. They also showed that the absolute MR effect in isotropic MR elastomers increases exponentially with increasing iron content below the CPVC, independent on the matrix material [7].

5.3 Influence of particle magnetization on the behavior of MREs

Domain dipole rotation in the presence of a magnetic field causes interparticle attraction. Maximum interparticle attraction and thus maximum magnetorheological effect is obtained by selecting a filler material with a high saturation magnetization M_s. Iron has one the highest saturation magnetization values of frequently used elements with $M_s = 2$ Tesla. Spherical carbonyl iron particles obtained from the thermal decomposition of iron pentacarbonyl are commonly used in MR materials. Iron has high permeability, low remanent magnetization and high saturation magnetization. High permeability and high saturation magnetization provide high interparticle attraction, and thereby a high MR effect. Low remanent magnetization is also recommended, as highly remanent particles tend to stick together when the magnetic field is turned off, and will therefore not yield a completely reversible MR effect. Alloys of iron and cobalt are known to have a slightly higher saturation magnetization (up to $M_s = 2.4$ Tesla) than pure iron and they have also been used in MR fluids [1, 6].

The magnetic properties of particles can be described by a magnetic induction versus magnetic field strength curve (B vs H). This is linear at small field strength H values, i.e., $B = \mu H$ where μ is the permeability of the material. For Fe, μ is typically in the range of $100\mu_0$ (permeability of free space). At high field strength values, the following equation is valid [29]:

$$B = \mu_0 \left(H + M_s \right) \tag{22}$$

where M_S is the saturation magnetization and $\mu_0 M_S \cong 2$ Tesla for Fe. However, small particles can start to saturate at lower field strength values than the bulk material. When measuring the MR effect as a function of the applied magnetic field strength, the MR effect does not increase as much with increasing field strength values above the magnetic induction of 0.55 Tesla for samples containing approximately 32 vol.% of iron as at lower field strength values [7]. Zhou has reported that in the system consisting of RTV silicone and 27 vol.% carbonyl iron, saturation occurs at about 0.8 Tesla [10].

In the current literature, two methods are presented for analyzing the magnetic interaction between the particles in the single-chain model. One is the point-

dipole model [3, 4], in which the local field and the sphere magnetization are considered as uniform. This model produces a field-dependent modulus proportional to the square of the applied magnetic field strength. The other method considers the subquadratic field dependence arising from the saturation of the magnetization near the poles of closely spaced pairs of spheres, which occurs at the applied field strength values well below the saturation magnetization. This approach yields a field-dependent modulus proportional to the applied magnetic field strength in the range from small to moderate field strength values [10]. The above-mentioned models consider the interaction between two nearby dipoles. In the following, a recently introduced model that takes into account the dipole interactions caused by all dipoles in the chain is presented [27].

In the MRE, each particle can be thought as a magnetic dipole with a dipole moment. The interaction energy between the dipole moments m_1 and m_2 separated by the distance r is [27]:

$$E_{12} = \frac{1}{4\pi\mu_0\mu_1}\left[\frac{\bar{m}_1 \bullet \bar{m}_2}{r^3} - \frac{3}{r^5}(\bar{m}_1 \bullet \bar{r})(\bar{m}_2 \bullet \bar{r})\right] \tag{23}$$

where μ_0 and μ_1 are the permeabilities of the vacuum and the MRE, respectively. For a dipole i the dipole moment is determined by

$$\bar{m}_i = \frac{4}{3}\pi a^3 \mu_0 \mu_1 \chi H_i \tag{24}$$

where a is the particle radius, χ is the magnetic susceptibility of the particle and H_i is the magnetic field strength at that point. The field experienced by the dipolar particle i is the resultant of the applied external field H_0 and the local field induced by the particles around the particle i [27]. For very long chains, the magnetic field of particle i in the chain can by expressed as

$$H_i = \bar{H}_0 + \sum_{j\neq i} H_j = \bar{H}_0 + 2\sum_{j=1}^{n}\frac{3\hat{r}_j(\hat{r}_j \bullet \bar{m}_j) - \bar{m}_j}{4\pi\mu_0\mu_1 r_j^3} \tag{25}$$

Supposing that the particle interactions occur only in the same chain and that particles are evenly distributed along the chains, then $r_j = jr$, where r is the mean distance between the particles i and j. When the chain is very long, it can be assumed that the particle moments are self-consistent, i.e. $\bar{m}_i = \bar{m}_j = m$. By substituting Eq. (25) into (24) and letting $C = \Sigma^n_{j=1}(1/j^3)$, the following equation is obtained [27]

$$m = \frac{4}{3}\pi a^3 \mu_0 \mu_1 \chi H_0 \left[\frac{1}{1-\left(\frac{4}{3}\right)\chi C\left(\frac{a}{r_0}\right)^3}\right]$$

(26)

In the chain-like structure, particles can be thought to form arrays that have similar properties as fibers in the composite matrix [9, 27]. Actually the fibers here are chains of separate particles and the chain stiffness is very sensitive to the amount of polymer in the gap between the particles. The magnetic force F_m between two spheres inside a chain can be calculated by finite element analysis and the corresponding magnetic stress in the matrix is [9, 38]:

$$\sigma_H = N_c \frac{F_m}{S} = \frac{3}{2}\phi \frac{F_m}{\pi a^2}$$

(27)

where N_c / S is the number of chains per unit cross section. [9, 27]. The mean distance between the particles changes in the magnetic field from the initial distance of r_0 to r. The corresponding shear strain can be obtained from the geometry of particle arrangement: $\gamma = \left(\sqrt{r^2 - r_0^2}\right)/r$. The increase of the shear modulus ΔG induced by external magnetic field is:

$$\Delta G = \frac{N_c F_m}{\gamma}$$

(28)

where γ is the shear strain. On the basis of these equations, the shear modulus increase caused by the magnetic field can be determined by the equation:

$$\Delta G = \frac{9}{8} \frac{\phi C m^2 (4 - \gamma^2)}{r_0{}^3 \pi^2 a^2 \mu_0 \mu_1 (1 + \gamma^2)^{7/2}} \tag{29}$$

which shows that the shear modulus change is quadratically proportional to the value of the dipole moment. However, the particles are assumed to be uniform and homogenous spheres that can be modeled as identical dipoles. They are also regarded as evenly arranged into chains in the isotropic matrix of the composite and the magnetic field is assumed to be static [27].

6. Applications of MREs

Elastomers with field responsive rheology hold promise in enabling simple variable and controllable stiffness devices. The applications for systems employing variable stiffness or resonance tunability are countless; among these are adaptive tuned vibration absorbers (TVAs), tuneable stiffness mounts and suspensions, and variable impedance surfaces.

Ford Motor Company has patented [2] an automotive bushing employing a MR elastomer. The stiffness of the bushing is adjusted based on the state of the automobile's power train to reduce suspension deflection and to improve passenger comfort. In the Ford Research Laboratory, applications of MR elastomers include automotive bushings and engine mounts, where significant changes in spring constant due to an applied magnetic field can be used to dynamically control stiffness and damping properties. Such tuneable components could for example minimize the effect of suspension resonances excited by torque variation caused by worn brake rotors by shifting the resonance away from the excitation frequency. Many suspension applications involve relatively large deflections at low frequencies (below 100 Hz). Toyota Central R&D Laboratory has also developed silicone gels containing Fe particles for tuneable engine mounts [1, 2, 3, 4, 13].

Significant changes in spring constant due to an applied magnetic field can be used to control stiffness and damping dynamically. For TVAs employing MR elastomers, the relative change in natural frequency can be calculated in terms of the relative change in the modulus as follows:

$$\frac{\Delta \omega}{\omega_0} = \sqrt{1 + \frac{\Delta G}{G_0}} - 1 \qquad (30)$$

where $\Delta G/G_0$ is the relative change in modulus and $\Delta \omega / \omega_0$ is the corresponding relative change in natural frequency. MR effect is shown to be substantial also at high frequencies up to kHz range. Therefore the MREs could also be utilized in constructing devices for noise and vibration control [5, 46].

In addition to the field dependent rheological response of these elastomer composites, utilization possibilities may also be found in their inherent anisotropic properties resulting from the particle structure. MR elastomers are anisotropic in terms of mechanical, magnetic, electrical and thermal properties [1]. However, these properties should be studied in detail in order to use these materials efficiently.

7. Aim of the work

The aim of this work was to increase the knowledge on the mechanical and viscoelastic properties of isotropic and aligned MREs. Application of external magnetic field can increase the stiffness of the MREs as shown in the literature review. However, in the literature contradictory results are presented concerning the influence of the magnetic field on the damping properties of MREs. The elastic and damping properties of isotropic and aligned MREs were studied to find the explanation for the contradictory results of previous studies. The changes of the shear modulus of the MREs with applied magnetic field have been reported extensively in the literature, but only in one study [39] the mechanical behavior of the MREs is examined in compressive loading. Nevertheless, one of the most important applications of the MREs would be as tuneable compressive elements and therefore the mechanical and magnetorheological properties of the MREs were studied in compressive loading.

The current modeling of the MREs is mainly based on the previous studies with the MR fluids. There are certain similarities how these two types of MR materials behave, but in elastomers the movement of the filler particles is more restricted than in fluids. In this study, the elastic properties of MREs have been characterized to reveal if the assumptions of the cubical particle structure used in MRF modeling are also valid with the MREs. The influence of the aligned particle structure was studied by varying the mutual loading and magnetic field directions during the dynamic testing of the aligned MREs.

8. Experimental procedures

In this study, isotropic and aligned silicone MREs containing 0 to 30 vol.% of carbonyl iron powder were prepared and characterized with different methods. Cyclic loading at resonance, dynamic compression testing and ultrasonic techniques were applied for characterizing the elastic and the vibration damping properties of the MREs. The damping properties and the elastic moduli of the isotropic and aligned MREs containing different volume fractions of iron filler were first studied without applied magnetic field to reveal the basic composite properties. The field-induced elastic moduli values and corresponding changes in damping properties were studied and compared to the zero-field values to find the optimum filler fraction for the maximal MR effect. The MRE properties were measured both at room temperature and at elevated temperatures. The experimental shear modulus values for isotropic MREs were analyzed and compared to the existing models for isotropic composite materials. In addition, the magnetization of the isotropic MREs containing 15, 20 and 30 vol.% of Fe was measured with a superconducting quantum interference device (SQUID).

Spring elements consisting of aligned and isotropic MREs with 30 vol.% of Fe were studied both without magnetic field and with increasing field strength in compressive dynamic loading. The dynamic stiffness and the loss factor values were calculated from the measured force-displacement loops. For compressive testing in magnetic field, a special coil device was designed so that the compressive load and the magnetic field direction could be applied parallel to the aligned chain direction in the MRE. The dependence of the MR effect on the testing frequency and strain amplitude was studied for exploring the possible use of the MREs in low-frequency structural applications with varying load and strain. In addition, the static stiffness of aligned MREs with 30 vol.% of Fe was measured as a function of the magnetic field strength.

9. Preparation of the MRE composites

9.1 Starting materials

The matrix materials in the studied magnetorheological elastomers were commercial Wacker Elastosil M4644 and M4601 silicones. These silicones were selected on the basis of preliminary studies with different elastomers (silicone, NR and SEBS elastomers). Elastosil M4644 and M4601 are two-component high strength polydimethylsiloxanes (PDMS) that vulcanize at room temperature. The silicones have different hardness values: M4644 has the Shore A hardness of 41 and M4601 has the Shore A hardness of 28. The silicone polymer (Me_2SiO) chains transform into three-dimensional networks via a cross-linking reaction, which allows the formation of chemical bonds between the adjacent chains. M4644 and M4601 silicones belong to the addition-curing elastomers. The addition occurs mainly on the terminal carbon atoms (β-addition) and is catalyzed by Pt or Rh metal complexes. The addition reaction yields no by-products like acetic acid and therefore no corrosion of carbonyl iron is expected in the composites. Another advantage of these silicones is that the molded samples do not shrink during curing. The PDMS have a low surface tension and are capable of wetting most surfaces. The stability and chemical neutrality of the system enables also the adhesive bonding to metals [16, 17].

As the filler material, spherical carbonyl iron particles (ISP-3700 Micropowder) were used. These were prepared by the thermal decomposition of iron pentacarbonyl. The particle size distribution was measured using a Lecotrac LT-100 laser particle size analyzer and it is presented in Fig. 9. Iron has one of the highest saturation magnetization values of metallic elements with $M_s = 2.1$ Tesla. It also has high permeability, low remanent magnetization and high saturation magnetization. High permeability and saturation magnetization are thought to provide high interparticle attraction and thereby a high MR effect. The low remanent magnetization is also recommended, because the highly remanent particles will stick together when the magnetic field is turned off. Thereby they will prevent the MR effect from being reversible [1, 6]. The magnetostriction of iron particles is also low [29].
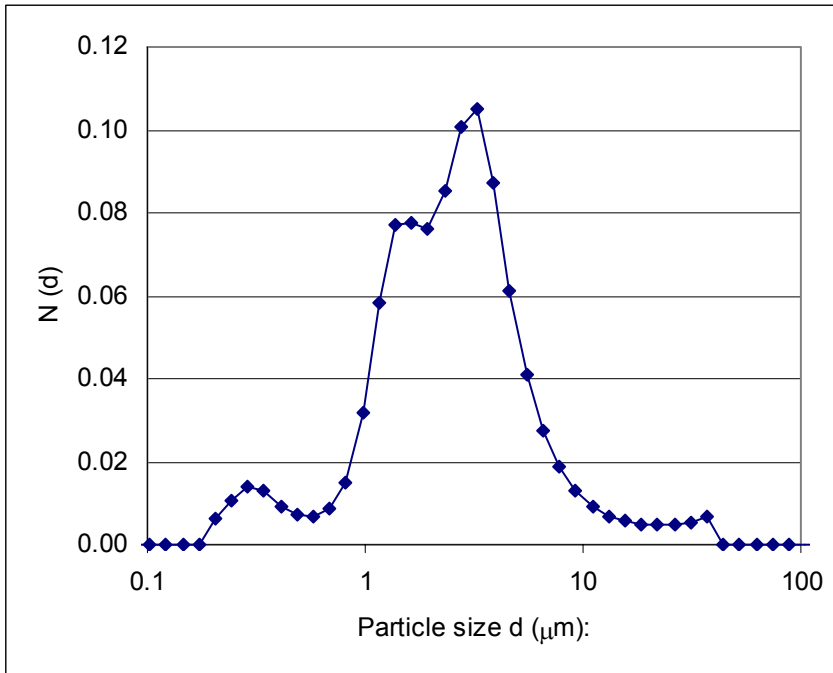
Figure 9. Particle size distribution of the carbonyl iron ISP-3700 powder used in the present work as measured by the Lecotrac LT-100 laser particle size analyzer.

9.2 Preparation of MRE samples for dynamic mechanical testing

Small rectangular MRE samples were prepared for the testing with the dynamic mechanical analyzer (DMA). Isotropic and aligned samples containing 5 to 30 vol.% of Fe were prepared from the silicone M4644 and samples with 30 vol.% of Fe from the silicone M4601. The two components A and B of the silicone matrix were first mixed together in ratio of 10:1 (M4644) and 9:1 (M4601) by kneading them together for several minutes. The dry iron particles were then gradually added to the silicone paste and mixed thoroughly in the same way. During the mixing, the paste was studied to ensure the deagglomeration of the iron particles.

Isotropic MRE sheets ($1.6 \times 100 \times 130$ mm) were prepared by pouring the homogenous silicone- iron-mixture into the lower part of the two-piece flat mold

and degassing the open mold at a vacuum of 1.33 Pa. Degassing was considered as completed when gas bubbles no longer emerged from the paste. The flat upper half of the mould was then placed on top and pressed approximately to a pressure of 4 MPa in a hydraulic press and the polymer was cured under pressure at room temperature for 20 hours. MRE samples containing aligned particle chains were prepared in the same way, except that the final curing was carried out under a static magnetic field strength of 0.13, 0.3 or 0.8–1 Tesla. A moderate magnetic field strength of up to 0.3 Tesla was used for aligning thin MRE sheets and 0.8–1 Tesla for aligning the cylindrical compression samples (height 20 mm, diameter 50 mm). Rectangular bar-shaped samples with varying width were cut from the prepared sheets. The length (7 mm) and the thickness (1.6 mm) of the rectangular samples were kept constant, while the width of the samples with different filler fractions was slightly varied (from 3 to 5 mm) to locate the resonance frequency in the available frequency range of the DMA. The prepared MREs were studied using SEM and optical microscopy to ensure the deagglomeration of filler particles and the complete degassing of the samples (no gas bubbles entrapped inside the cured material).

Before polymerization (in catalyzed state) the viscosity of the silicone is quite low (50 Pas of M4644 and 20 Pas of M4601). Therefore, the magnetized particles can slightly move in the silicone matrix and align themselves along the magnetic field lines. MRE samples were prepared with iron contents varying from 5 to 30 vol.% to find the optimum filler volume fraction for maximizing the MR effect. The volume fraction of the Fe particles was restricted to max. 30 vol.% due to the possible degradation of the mechanical properties of the composite with higher filler fractions [6,7].

Figs. 10 and 11 illustrate the BEI mode SEM images of the freeze-fractured surfaces of the isotropic and aligned MREs containing 30 vol.% of iron, respectively. In Fig. 10 the particles have a random distribution whereas in Fig. 11 the chains of aligned particles can be seen.
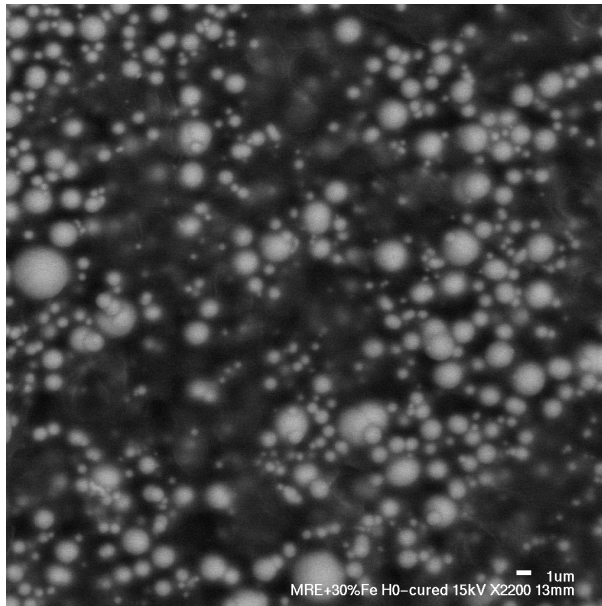
Figure 10. Microstructure of an isotropic MRE with 30 vol.% of Fe. A BEI mode SEM image taken from the freeze-fractured surface. Magnification 2000×.
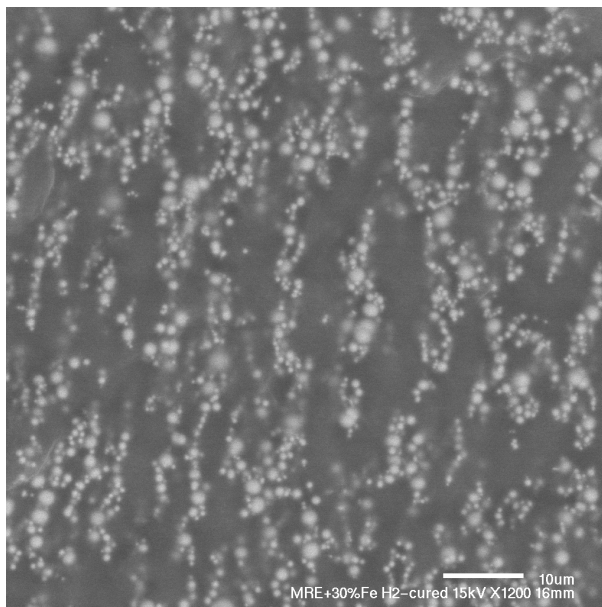

Figure 11. Microstructure of an aligned MRE with 30 vol.% of Fe. A BEI mode SEM image taken from the freeze-fractured surface. Magnification 1100×.

9.3 Preparation of MRE samples for compression testing

The mixture of the silicone M4644 or M4601 with carbonyl iron powder (30 vol.%) was prepared similar to the DMA samples. The homogenous mixture of silicone and iron was poured into a cylindrical steel mould with the inner diameter of 50 mm and the height of 20 ($\pm$ 2) mm and degassed in a vacuum. The isotropic MREs were cured without an applied magnetic field while the aligned MREs were subjected to a strong, uniaxial magnetic field of nearly 1 Tesla during the curing process.

The magnetization equipment used for aligning the samples consisted of a magnetization coil with 7000 turns and a magnetically soft Armco iron core. The upper and lower cylindrical mould pistons made of Armco iron were connected to the core with iron guide bars. The upper guide bar was designed so that the upper piston could move freely in the axial direction. The MRE mixture was compressed inside the mold with the upper piston into the preferred molding volume and the magnetic field was applied during the compression. The magnetic field strength inside the mold was measured using a gaussmeter (MG-5DAR, Walker Scientifitic Inc.). The magnetic field strength between the pistons during the curing was measured to be in the range of 0.8 to 1 Tesla. Aligned and isotropic cylindrical samples with 30 vol.% of Fe were prepared for compression testing. For comparative purposes unfilled silicone samples were also prepared in the same way. Steel plates (thickness 2 mm) with the diameter of 50 mm were bonded to both ends of the samples using the silicone paste as an adhesive.

10. Dynamic and static measurements

10.1 Analysis of the dynamic systems

The dynamic properties of MREs were studied in cyclic loading. In the DMA, an oscillating force is applied to the samples, which are deformed sinusoidally in single degree of freedom. The essential physical characteristics of any linearly elastic structural system subjected to dynamic load include its effective mass, its elastic properties (flexibility or stiffness), its energy-loss mechanism or damping, and the external source of excitation or loading [24]. A schematic presentation of an idealized system with a single degree of freedom and the equilibrium of forces are given in Fig. 12. The system is the so-called Voigt model, consisting of a spring and a dashpot in parallel coupling.
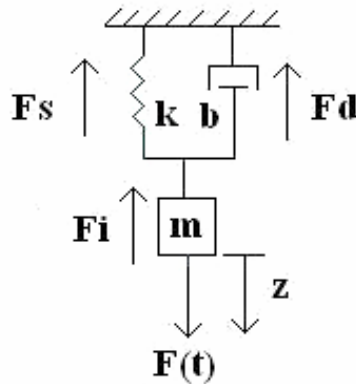

Figure 12. The idealized dynamic system with single degree of freedom and the equilibrium of forces. The symbols are: displacement z, *spring constant* k, *viscous damping constant* b *and the mass of the system* m. *The forces acting in the system are: applied load* F(t), *inertia force* F_i, *damping force* F_d *and the elastic spring force* F_s.

The load of the specimen must be low to ensure that the linear viscoelasticity is valid. Assuming that the MRE is subjected to an oscillatory strain with sufficiently small amplitude, the displacement may be expressed by [18, 19, 20]

$$z = z_0\, e^{\,i\omega t} \tag{31}$$

where z_0 is the maximum displacement amplitude and ω is the angular frequency. The equation of motion for a dynamic system with viscous damping and subjection to a harmonic input force is defined as:

$$m\,\ddot{z}(t) = -b\,\dot{z}(t) - k\,z + F_0\, e^{\,i\omega t} \tag{32}$$

where m, b and k are the effective mass, viscous damping constant and the spring constant of the system, respectively. The term on the left expresses the acceleration of the system, while the first term on the right is the velocity of the system with assumed damping. For analyzing the data obtained from the DMA experiment, the equation must be solved in relation to the displacement amplitude. By inserting the Equation (31) to Equation (32), the following form can be obtained:

$$z_0 = \frac{F_0 / k}{\sqrt{\left(1 - \dfrac{\omega^2}{\omega_0^{\,2}}\right)^2 + \left(\dfrac{b\,\omega}{k}\right)^2}} \tag{33}$$

As the natural frequency ω_0 is defined as $\omega_0^{\,2} = k/m$, both the viscous damping constant b and the spring constant k can be obtained from Equation (33) if the amplitude is known as a function of the frequency. With the resonant technique, the frequency-response curve of the sample can be constructed as follows: the harmonic load is applied at different closely spaced frequencies, which span the resonance frequency, and for each frequency the resulting displacement amplitude is measured. The measured amplitudes are then plotted as a function of the applied frequency [24]. The resonance curve can then be fitted to the equation of motion. A typical frequency-response curve of a moderately damped system is shown in Fig. 13. In the figure z_0 corresponds to the static displacement of the system, which is produced by the application of the static force F_0, z_R is the maximum displacement at resonance frequency, and β represents the ratio applied load frequency over the natural resonance frequency. When the frequency ratio $\beta = 1$, the system is in resonance [20, 24].
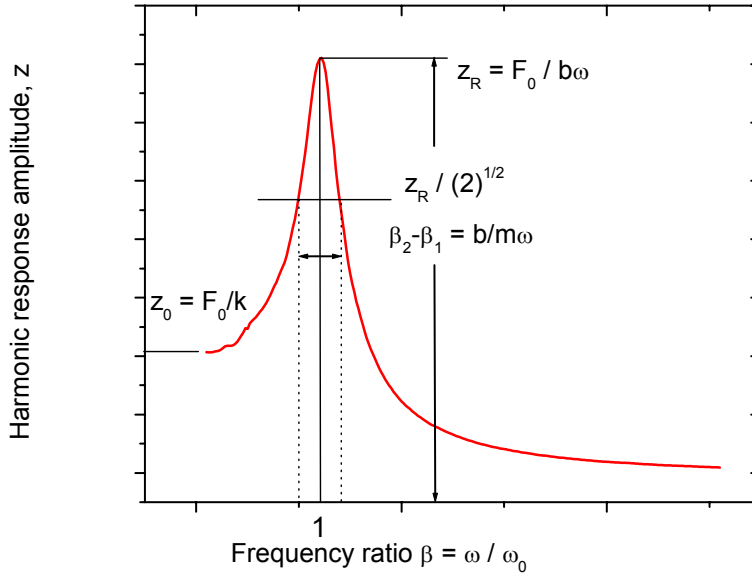
Figure 13. Frequency-response curve of a moderately damped system. For the definition of the symbols see the text.

The characteristics of viscoelastic materials are influenced by several parameters, such as frequency, temperature, dynamic strain rate, static preload, time dependent effects (creep and relaxation), aging and other irreversible effects. The most important parameters include the effects of frequency and temperature. Viscoelastic materials may exist in various states within the broad temperature and frequency ranges they are used. The states are typically referred as the glassy, transition, rubbery and flow states and the viscoelastic materials behave differently depending on their state during testing [18].

The silicones have a very low glass transition temperature. For polydimethylsiloxane-based (PDMS) elastomers $T_g \approx$ -120°C or below. The measurements on Elastosil M4644- and M4601- based MREs were carried out in the temperature range from room temperature up to 140 ºC and in the frequency range from 1 to 51 Hz. The test temperature is well above T_g (in the rubbery regime) where G' is independent on temperature, and G'' decreases slightly with increasing temperature. The increase of the frequency of the measurements has the equivalent effect as the increase of the 'apparent' glass transition temperature. However, for a frequency of 50 Hz this shift is small and the present data in the regime of 1–50 Hz should be largely independent on frequency.

Cyclic loading was also used for studying the MRE spring elements in compression. The mechanical properties of the MREs were characterized in dynamic cyclic compression both passively (without the magnetic field) and with increasing magnetic field strength. The influence of the testing frequency and strain amplitude on the dynamic stiffness and damping was studied.

On the basis of the force-displacement loops measured in harmonic loading, the dynamic stiffness and the loss factor can be calculated by determining the energy loss per cycle [16]. The slope k of the major axis of the force-displacement hysteresis loop indicates the stiffness while the area D captured inside the loop describes the damping in the system. The area D captured within the hysteresis loop is equal to the dissipated energy per cycle during the harmonic straining of the material. The relationship between the material damping and the loop area can be defined as:

$$D = \int F dx = \int_0^x \left(kx \pm \eta\, k\, \sqrt{\left(X^2 - x^2\right)} \right) dx = \pi\, \eta\, k\, X^2 \tag{34}$$

The stiffness is defined by the spring constant k and the damping properties by the loss factor η. For calculating these parameters, a Labview program was used for automatic determination of the average value and standard deviation of both the spring constant and loss factor from several consecutive force-displacement loops.

The viscous damping ratio ξ or the loss factor η are often used instead of the viscous damping constant b. The damping ratio and loss factor are dimensionless material parameters, while the damping constant b also depends on the dimensions of the sample and describes the rate of damping of the system (the damping force required to move a body with a certain velocity). The damping ratio is defined as the ratio of the actual damping to the critical damping. Both the damping ratio and damping constant are giving information on the damping behavior of the vibratory system. For low levels of damping and within the linear viscoelasticity region of the material, the different measures of damping can be equated using the following relationship.

$$Tan\ \delta = \eta = 2\,\xi = \frac{b}{m\omega_0} \tag{35}$$

The damping ratio is often presented as a percentage or as the fraction of the critical damping, %Cr. A system is classified as underdamped if $\xi < 1$, critically damped if $\xi = 1$ and overdamped if $\xi > 1$. Vibratory motion will only exist in an underdamped system.

10.2   3-point bending tests

The dynamic characteristics of MRE samples prepared with different filler fractions were measured using a Perkin Elmer dynamic mechanical analyzer (DMA). The Perkin Elmer DMA 7 can be used for the characterization of the mechanical behavior of a broad range of materials from soft elastomers to hard composites and ceramics. The DMA runs were carried out as frequency scans with fixed static and dynamic forces at room temperature and as a function of the temperature. Static and dynamic forces are used simultaneously in the measurements. The static force ensures that the vertical exciter stays in contact with the specimen during the analysis. The sinusoidal dynamic force component is added on top of the static force. The force and the dimensions of the rectangular bar-shaped samples were optimized in order to locate the resonance frequency ω_0 of the MRE samples in the available frequency range of the device (1–51 Hz), preferably $\omega_0 / 2\pi \approx 25$ Hz. The optimum combination of forces was $F_{stat} = 110$ mN and $F_{dyn} = 50$ mN, which was used for all the MRE samples. The sample dimensions were length 7 mm, thickness 1.6 mm and the width was varied from 3 to 5 mm.

With DMA, soft elastomers are usually measured in compression. Due to the increasing stiffness of the samples with higher filler fractions and the limitation of the available frequency range, 3-point bending was used in this study. It has been used successfully for measuring the dynamic properties of silicone elastomers [22]. For the actual measurements a non-magnetic stainless steel measuring system was used where the sample holder had a width of 5 mm between the supports. For the measurements with applied magnetic field, a permanent magnet was attached to the system with poles on both sides of the measured sample. The distance between the sample and the poles was minimized (2 mm on each side) but it was ensured that the sample was not touching the poles during the measurement. The magnetic field strength H of two different magnets connected to the sample holder was measured with a gaussmeter (Lakeshore 421) and the results were 0.13 and 0.3 Tesla,

respectively. Some aligned MREs with higher filler fraction could not be measured with 0.3 Tesla due to the movement of the sample in magnetic field.

To check the system, pure silicone was measured without an applied field and with the two different magnets. The measured resonance curves with and without magnetic field were found to be identical. The system losses were evaluated by running a frequency scan for a thin strip of elastic stainless steel, which showed a very sharp resonance peak as compared to the silicone and the MREs. Fig. 14 shows schematically the measuring system for rectangular samples with the permanent magnet attached.

Aligned MREs were measured in two directions: oscillating force parallel to the chains (Direction 1.) and perpendicular to the chains (Directions 2. and 3.). In all cases, the magnetic field direction was perpendicular to the oscillating force as shown in Fig. 15.
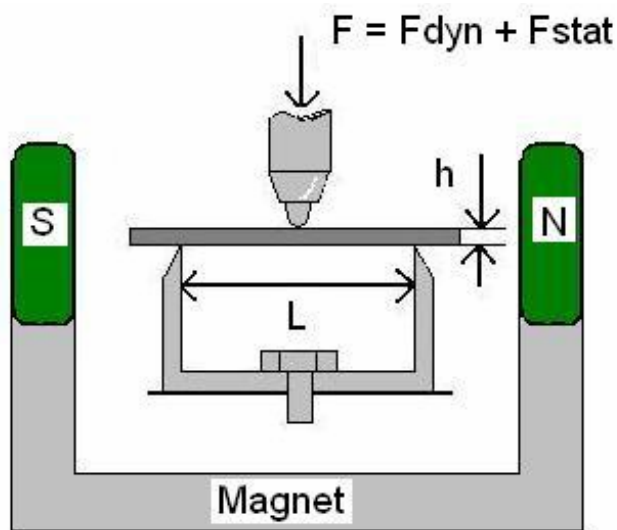

Figure 14. 3-point bending DMA measurement system for rectangular samples with the permanent magnet. L *(5 mm) is the distance between the supports and* h *(1.6 mm) the height of the sample. The width of the sample was varied from 3 to 5 mm and the distance between the poles and the sample was varied from 2 mm to 3 mm.*
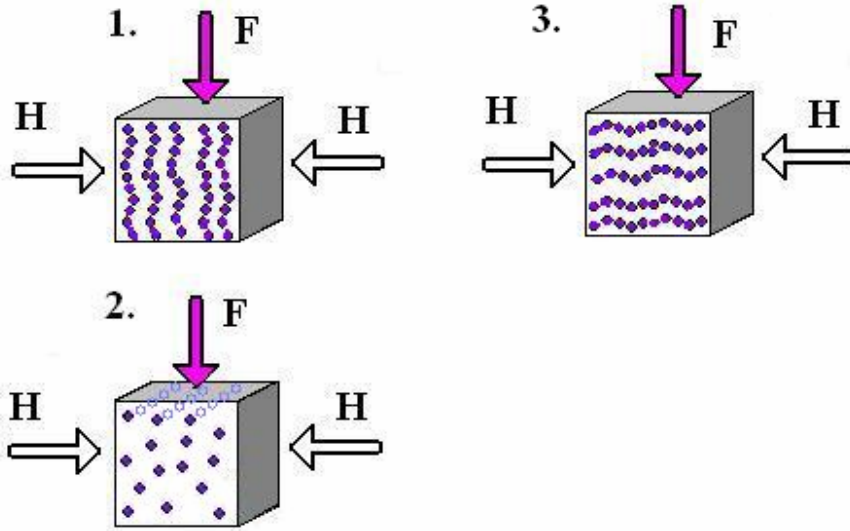
Figure 15. Measuring directions of aligned MREs in the DMA measurements. Oscillating force is 1. parallel to the chains, 2. and 3. perpendicular to the chains. In the Direction 2. the magnetic field direction is perpendicular and in the Direction 3. parallel to the particle chains.

10.3 Compression testing

For the static and dynamic compression testing of the MR spring elements a servohydraulic universal testing machine (Instron 82502) with the maximum force of ± 100 kN was used. The maximum usable frequency range of the testing machine was from 10 to 30 Hz, depending on the displacement amplitude of the control signal (± 0.5- ± 2 mm). The data was collected digitally using the Microstar Laboratories iDSC816 digital signal conditioning board. The force and displacement were measured in the time domain and transformed to the digital frequency domain by using the fast Fourier transform (FFT) algorithm.

Spring elements consisting of a cylindrical MR elastomer were measured both passively and with the applied magnetic field. The spring elements were subjected to dynamic compressive loading, which fluctuated around the mean level and the control of the compressive strain amplitude varied the mean level of loading. The strain amplitude and frequency were varied in the testing. In the

first stage of measurements, sinusoidal load was applied in the frequency range from 0.5 to 15 Hz at a rate of 0.1 octaves per minute with constant strain amplitude. In the second stage of the measurements a constant frequency of 1 Hz was applied during testing and the strain amplitude was varied accordingly. The working principle of the spring element is presented in Fig. 16 a) and the testing apparatus in Fig. 16 b).
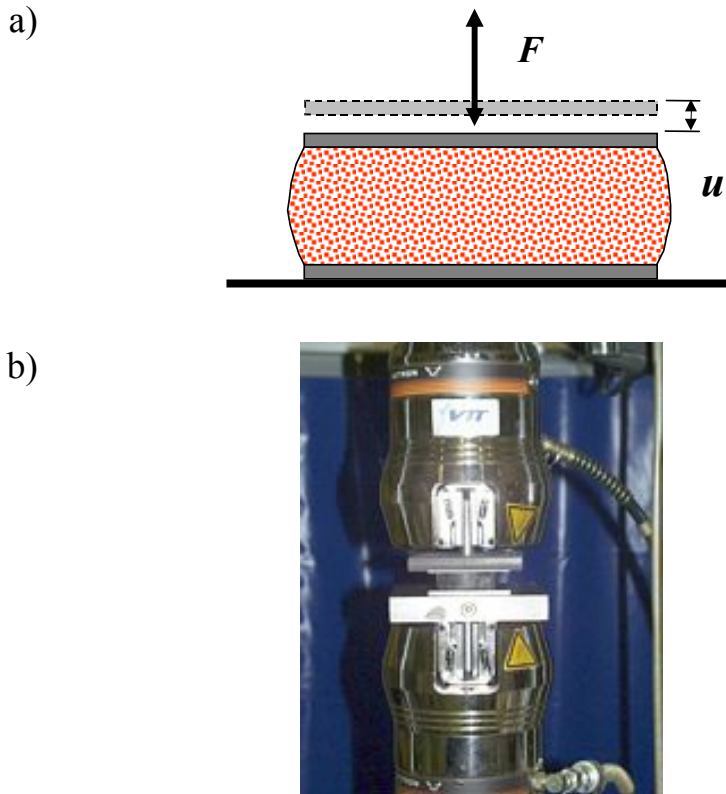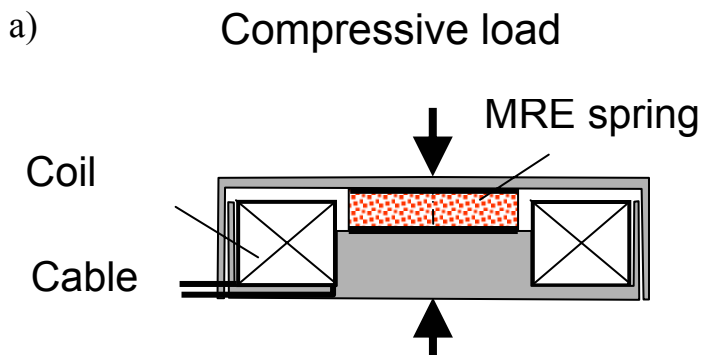

Figure 16 a) Schematic presentation of the MRE spring element, b) the testing apparatus with the sample inserted.

For testing under the magnetic field a compressive coil device with an operational amplifier power supply (Kepco BOP) was added to the testing machine. The magnetic coil device was designed so that the spring element placed inside the coil was a part of the closed magnetic circuit. During the compression testing the magnetic field was directed through the MRE spring element along its cylinder axis (in the chain direction of aligned MREs). The

design of the coil device is shown in Fig. 17 a) and b). The coil device consisted of a bottom steel core and a moving top cover with a central steel plate for directing the load on the sample. Thin copper strip was wound around the bottom core. When the sample was placed inside the bottom core with the top cover closed, the coil current produced a magnetic field through the sample. DC current up to 16 A was used for producing the magnetic field of 0.5 Tesla (140 W) in an empty coil device. The strength of the magnetic field inside the coil device was further increased by the MRE spring acting as an iron core.
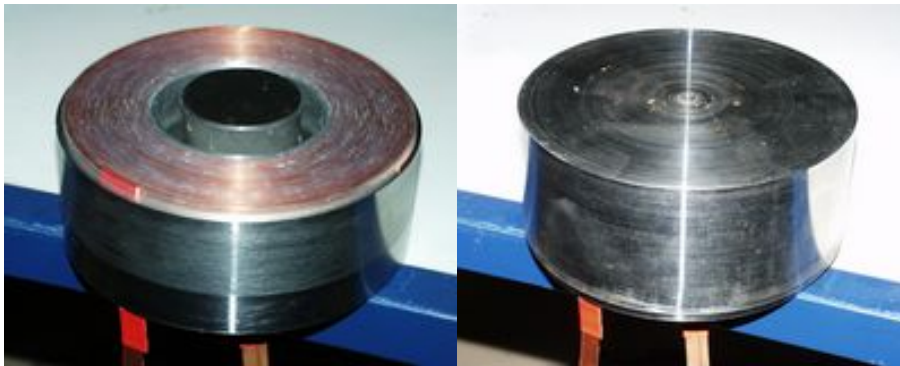
a)

b)

Figure 17. (a) Schematic presentation of the magnetic coil device with MRE (b) MRE spring element inside the magnetic coil device with the top cover open (left) and closed (right).

The magnetic field strength H inside the coil device was measured using a gaussmeter near the sample surface before testing. It was noted that for the maximum current (16 A) used in the measurements the field strength H inside the coil device varied with the permeability of the MRE. For aligned MREs with 30 vol.% of Fe the field strength H inside the coil device was measured to be 0.85–0.89 Tesla. For isotropic MREs with 30 vol.% of Fe the field strength was 0.77 Tesla and for the unfilled silicone 0.45–0.47 Tesla, which was nearly the same as the value measured for an empty coil. The magnetic permeabilities measured using the stationary-coil method were $\mu_I = 2.60$ for the isotropic and $\mu_A = 3.34$ for the aligned MREs with 30 vol.% of Fe. The permeability was measured along the cylinder axis of the MRE (in the chain direction in aligned MREs).

During the compressive testing it was noticed that when the magnetic field strength was increased the coil device itself added some compressive load on the MRE thus increasing the prestress on the MRE spring. This was due to the magnetic steel cover that was used for closing the magnetic circuit. In order to obtain correct values at higher applied magnetic field strength values, adding non-magnetic stainless steel piston acting on the MRE spring element modified the coil device. In this second version of the coil device, the magnetic field was influencing only the MRE similarly as in the DMA measurements. In the following, the two different coil devices are denoted Coil 1. and Coil 2., respectively.

11. Results

11.1 Results of the DMA measurements

The dynamic stiffness and damping values of isotropic and aligned MREs with M4644 silicone matrix and varying iron content were obtained from the DMA measurements carried out in resonance. The isotropic MRE samples were first measured without an external magnetic field. The measured curves (Figs. 18 and 19) show that the dynamic stiffness decreases near the resonance. The dynamic stiffness generally increases with increasing frequency; this behavior is common to most elastomers [18]. A typical resonance curve measured for an isotropic MRE with 30 vol.% of Fe is shown in Fig. 18. The size and the shape of the resonance peak describe the stiffness and damping of the material, respectively. When more damping is present, the resonance peak is broader and its peak value smaller as compared to materials with less damping. The measured data was fitted to the equation of viscoelastic motion (Equation (29)) and the viscous damping constant b, damping ratio ξ and the spring constant k were calculated for each sample.

The same samples were then measured under the influence of the magnetic field. The resonance curve of an isotropic MRE with 30 vol.% of Fe as studied under external field strength of 0.13 Tesla is shown as the lower curve in Fig. 18.
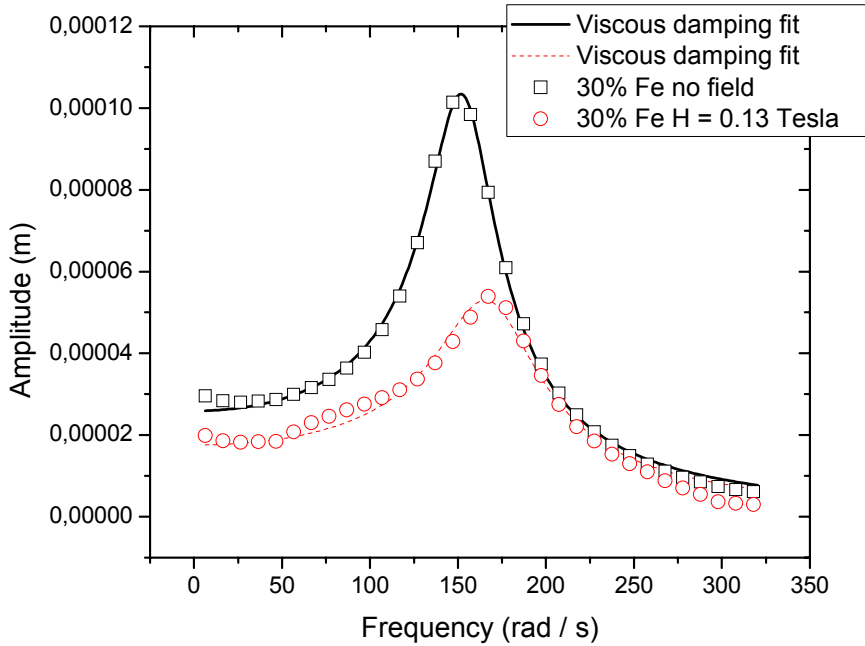
Figure 18. DMA frequency scan results for an isotropic MRE with 30 vol.% of iron. The results are shown with fitted viscoelastic model and they were measured without the magnetic field and with the field strength H of 0.13 Tesla.

The aligned MRE samples were studied using the same technique in both parallel and transverse directions of the aligned structure as described in Fig. 15. Aligned MREs were first measured without the magnetic field in Direction 1 (Fig. 19, upper curve). It was noted that the resonance peaks of aligned MREs were shifted to higher frequencies as compared to the resonance peaks of isotropic MREs containing the same amount of filler. As compared to the isotropic MREs the peak values were generally smaller, indicating that the aligned materials were stiffer in the chain direction than the isotropic MREs with the same amount of filler, when the external load was applied in the chain direction. When studied under magnetic field, the maximum values of the resonance peaks were further reduced in all samples. In Fig. 19 the upper curve is the zero-field resonance curve of an aligned MRE containing 30 vol.% of Fe measured in Direction 1 and the lower curve is the same sample measured under external field of 0.13 Tesla. The measured zero-field resonance peak leans backwards. This is an effect that is obtained in mechanical systems where the stiffness decreases with strain amplitude [33].
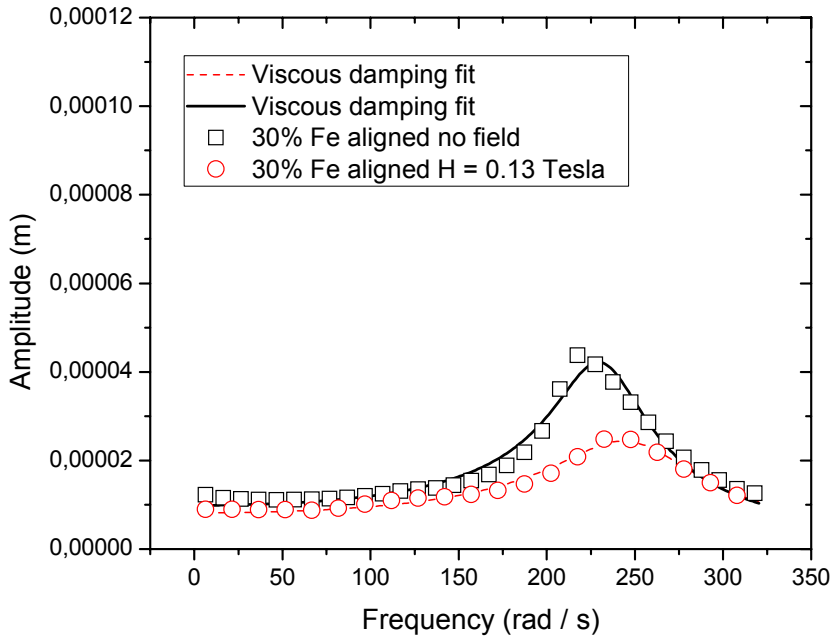
Figure 19. DMA frequency scan results of an aligned MRE with 30 vol.% of iron as measured in Direction 1 (see Fig. 15). The results are shown with fitted viscoelastic model, and they were measured without the magnetic field (upper curve) and with the field strength H *of 0.13 Tesla (lower curve).*

The viscous damping constant b was calculated for each studied material in order to reveal how the damping rate and consequently the damping force opposing the motion are changed with increasing filler content and magnetic field. Fig. 20 shows the average damping constant b of isotropic MREs with varying filler fractions as studied both passively and with the external magnetic field. Performing three to five separate measurements for the samples of each MRE material with different filler fractions and calculating the average values of b obtained the average values. The same statistical approach was used for defining the damping ratios and spring constants.

When measuring the isotropic MREs without an external field, only very small changes in the damping constant *b* with increasing filler volume fraction were detected. The value of the constant *b* stayed on the level of about 3 Nsm^{-1} when the filler volume fraction was increased from 5 to 30 vol.%. This was the same value as measured for the basic silicone. However, when applying an external

magnetic field, the values of *b* were clearly increased when the filler fraction exceeded the value of 15 vol.%. When the filler content was 27 vol.%, the average value for *b* as measured with the magnetic field strength of 0.3 Tesla was almost twice the initial value, between 5–6 Nsm^{-1}. With 27 to 30 vol.% of the filler the damping constant also increased when the field strength was increased from 0.13 to 0.3 Tesla indicating tuneability in magnetic field.
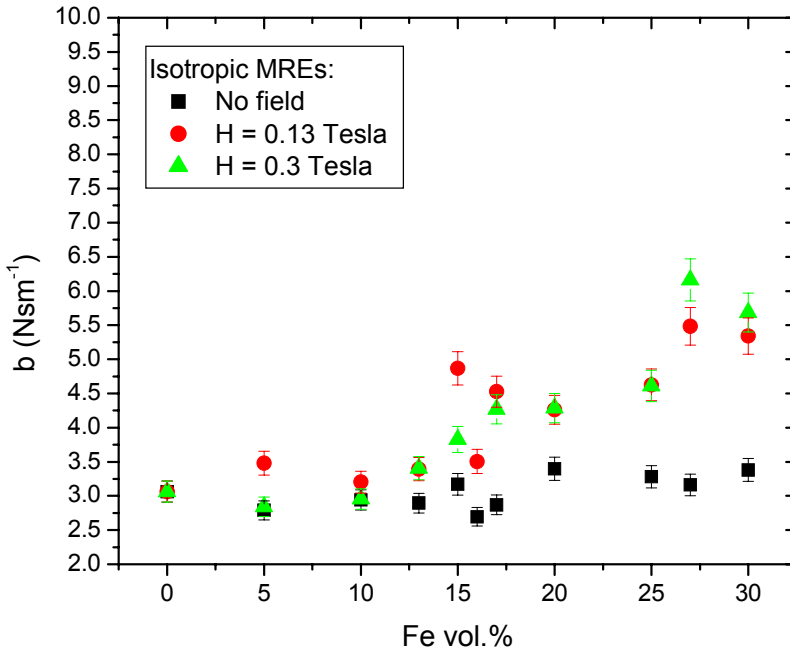

Figure 20. Measured average viscous damping constant b *of isotropic MREs as a function of the filler content. The damping constant was measured both without magnetic field and with the field strength* H *values of 0.13 and 0.3 Tesla.*

The average viscous damping constant *b* of the aligned MREs was studied similarly. The average values measured in parallel (Direction 1.) and perpendicular (Direction 2.) directions to the aligned particle chains are presented in Fig. 21. For the aligned MREs measured passively in Direction 1, the values of *b* increase from the initial value of about 3 Nsm^{-1} (no filler) up to about 6 Nsm^{-1} for 20 vol.% of Fe and decrease gradually after that with increasing filler content. When measured with external field, the values of *b* start to increase with increasing filler content after 15 vol.% of Fe. The increment of *b* in magnetic field (about 2 Nsm^{-1}) is almost constant between 17 to 30 vol.% of Fe.

When measured passively in Direction 2, the values of *b* are in the same range as in dir. 1. The influence of magnetic field on *b* is noted in this direction when the volume fraction of Fe exceeds 15%. However, in Direction 2 the maximum values and the difference in the values of *b* as measured both passively and with the magnetic field are somewhat smaller than those measured in Direction 1. When compared to isotropic MREs with the same filler fraction, it can be deduced that the chaining of the filler particles increases the damping rate in the composite material. The values of *b* are also increasing with higher filler fractions up to 20 vol.%. However, at filler fractions exceeding 27 vol.% the damping rate will start to decrease again when measured both passively and with the magnetic field.
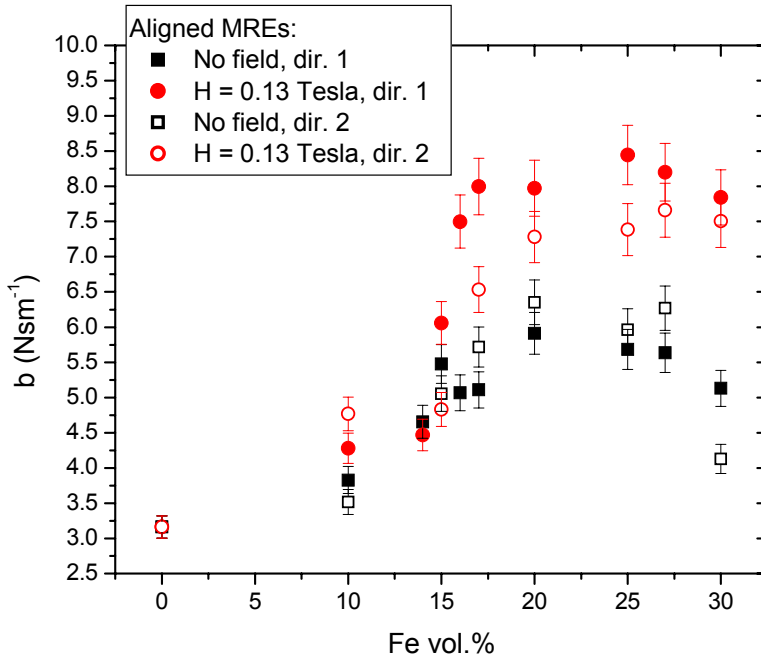

Figure 21. Average viscous damping constant b *of aligned MREs versus the filler content as measured in Directions 1 and 2 (see Fig. 15). The damping constant is measured both without the magnetic field and with the field strength* H *of 0.13 Tesla.*

The equation of motion was fitted to the measured data for isotropic MREs and the average viscous damping ratio ξ was calculated. The ξ value does not depend

on sample dimensions and it can be used for describing the energy dissipation by the system. In Fig. 22 it can be seen that the average damping ratios of isotropic MREs measured without field are somewhat lower than those of the unfilled silicone. The values of ξ are quite small, ranging from 0.16 to 0.12 for MREs with higher filler fractions. When applying magnetic field, the damping ratio ξ is increasing with the filler fractions exceeding 15 vol.%. The maximum value of about 0.26 is obtained at 27 vol.% of Fe by applying the field strength H of 0.3 Tesla. The difference between the damping ratio values measured passively and values measured with the applied magnetic field was also maximal with the filler content of 27 vol.%.
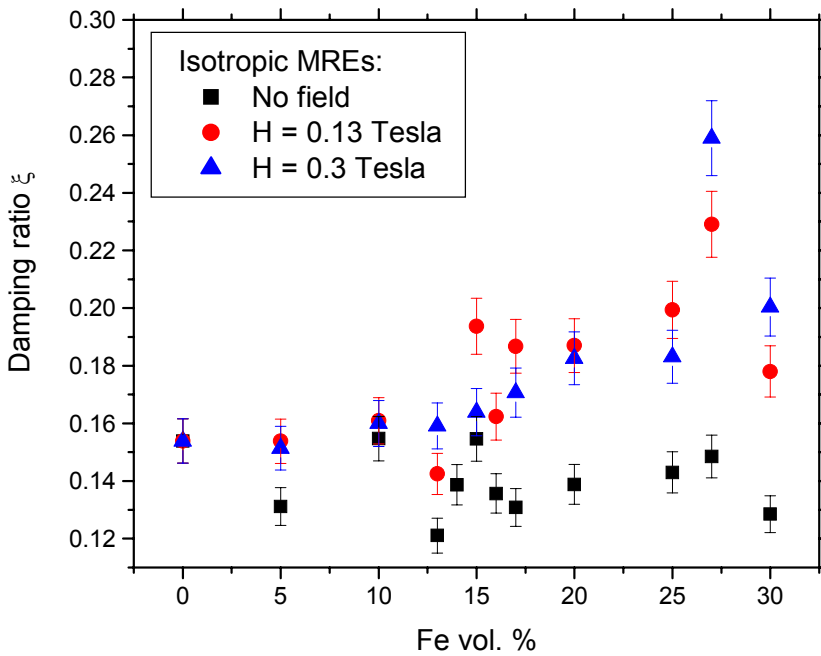

Figure 22. Calculated average viscous damping ratio ξ of isotropic MREs as a function of the filler content. The damping ratio is measured both without the magnetic field and with the field strength values of 0.13 and 0.3 Tesla.

The peak value measured for the damping ratio at the filler content of 27 vol.% for isotropic MREs can be explained on the basis of the finite element analysis by Davis [4]. He suggested that the optimum filler particle volume fraction, where the interaction between the particles is at strongest is 27 vol.%. The

particles are assumed to be arranged in a cubical structure, which in our case is formed simply by packing the particles and matrix polymer under pressure in the mould without the applied magnetic field. The optimal packing situation changes when the particle density increases or decreases. In his analysis, Davis also assumed that the matrix elastomer is isotropic. This is the case in isotropic MREs, where the filler particles with surrounding elastomer shell are distributed randomly and homogeneously in the composite.

The damping ratio values calculated for aligned MREs are presented in Fig. 23. For aligned MREs in Direction 1 the passively measured damping ratios were generally in the same range as those obtained for isotropic MREs. The average value of ξ was about 0.12. This value was more exact for aligned MREs than for isotropic MREs, where the zero-field ξ oscillated between the values of 0.12 (MREs with higher filler fractions) and 0.16 (pure silicone). The oscillating value is due to the random particle distribution in the isotropic MREs.

The values of the damping ratio of the aligned MREs measured in Direction 1 in magnetic field increased radically after 15 vol.% of Fe and the maximum value of about 0.20 was found between 20 and 30 vol.% of Fe. With this filler content, the relative change in the damping ratio due to the applied magnetic field was quite constant. When measured in Direction 2 passively, the damping ratio increased up to 20 vol.% of Fe with a maximum value of 0.22, and decreased slightly after that. When measured with magnetic field in Dir. 2, the damping ratio values were somewhat higher for all filler volume fractions and the maximum values of 0.24–0.28 were obtained in the range of 20 to 30 vol.% of Fe. However, the increase in damping ratio in magnetic field when measured in Direction 2 was much smaller than that measured in the Direction 1. On the basis of these measurements it is evident that the chain-like particle structure can dissipate more energy passively than the isotropic material with the same filler fraction. However, the vibration damping behavior is strongly directional in aligned MREs.
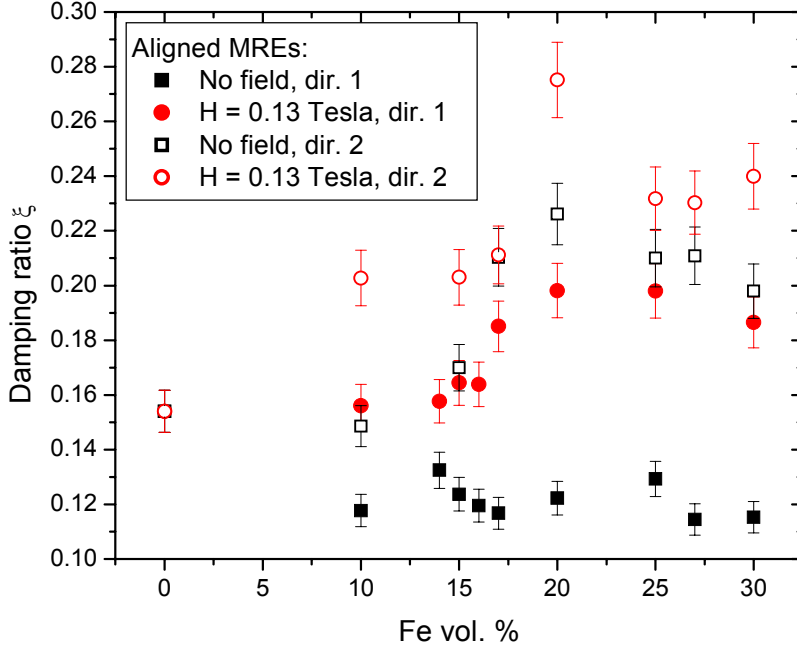
Figure 23. Calculated average viscous damping ratio ξ of aligned MREs as a function of the filler content, when measured in Directions 1 and 2 (see Fig. 15). The damping ratio is measured both without the magnetic field and with the field strength H *of 0.13 Tesla.*

The measured damping ratio of the silicone matrix was slightly decreased with iron addition. To some extent the viscoelastic behavior of silicone is modified by the addition of rigid filler particles as can be seen from the results obtained for isotropic and aligned MREs measured in Direction 1. On the contrary, the alignment of the particles increases the damping ratio remarkably when the dynamic loading is subjected on the particle chains. In aligned MREs the damping behavior is strongly directional with filler contents exceeding 15 vol.%. With applied magnetic field the damping can be increased only slightly in Direction 2 while in Direction 1 the increase is quite remarkable.

The difference $\Delta\xi$ ($\Delta\xi = \xi_M - \xi_P$) between the passively measured values ξ_P of the damping ratio and the values ξ_M measured under the magnetic field strength of 0.13 Tesla for isotropic MREs and aligned MREs in Directions 1 and 2 is presented in Fig. 24. In the figure it can be seen that the maximum relative

difference in damping is obtained when the filler fraction is 27 vol.% of Fe for both isotropic MREs and aligned MREs measured in Direction 1. The optimal filler fraction for maximal energy dissipation in this model system is 27 vol.%.

The relative difference in damping of the MREs with 27 to 30 vol.% of Fe is on the same level for isotropic MRE and aligned MRE when measured in the chain direction. When measured in Direction 2 the difference in damping between the zero-field values and values measured with applied magnetic field is decreasing after 20 vol.% of Fe and is very small at 25 to 30 vol.% of Fe. The explanation for this is that in Direction 2, the damping ratio is initially higher with filler fractions exceeding 20 vol.% and cannot be increased remarkably by the magnetic field. The increase is only about 0.01–0.02, which is also reported in other studies [7, 10]. The difference in damping is quite the same for all the studied MREs below 20 vol.% of Fe but the alignment of the particles is clearly influencing the damping with higher filler fractions.
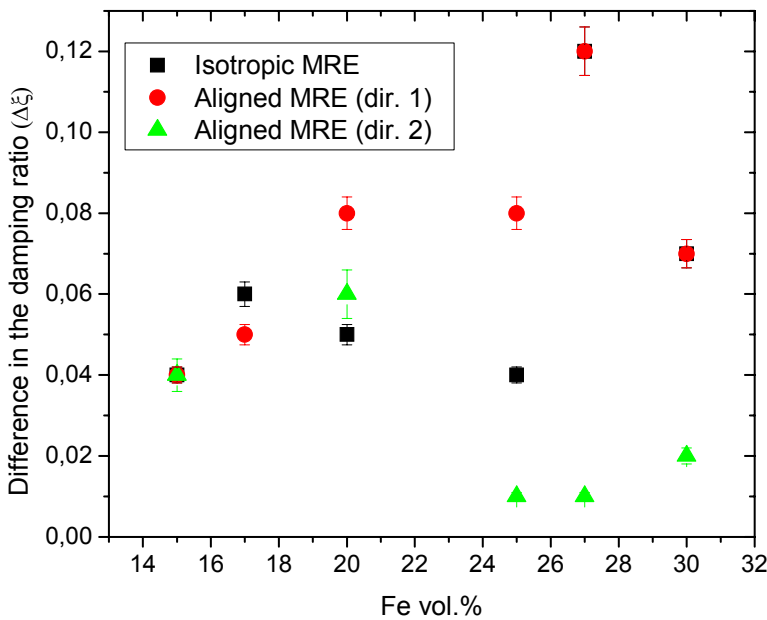

Figure 24. Difference in the damping ratio (Δξ) between the passively measured values and the values measured with the magnetic field strength of 0.13 Tesla for both isotropic MREs and aligned MREs measured in Directions 1 and 2 (see Fig. 15).

McKnight *et al.* [47] have characterized aligned polymer composites filled with magnetostrictive Terfenol-D particles. They have found that the damping produced by a specimen containing particles aligned perpendicular to the direction of loading was substantially smaller than the damping when the particles were aligned in the loading direction. They have suggested that in the chain direction particle chains support most of the stress and this additional stress allows the magnetization jumping in magnetostriction to occur in a larger fraction of particles than in direction perpendicular to the chains. The application of stress along one crystal plane lowers the energy barrier causing movement of the magnetic moment within the material. At a critical stress level, the magnetization may "jump" from one stable orientation to another, in a non-reversible energy absorption process. In our case, the magnetostriction effect is quite small in Fe particles when compared to Terfenol-D alloy but the same anisotropic damping behavior is observed in aligned MRE composites. In the aligned MREs with Fe filler, the difference in damping when measured in perpendicular directions is caused by the characteristic columnar structure and the consequent movement of the particles in external magnetic field when subjected to dynamic loading.

The average values of the spring constant k were also calculated for the isotropic and aligned MREs by fitting the equation of motion to the measured data. Without applied the magnetic field, the measured values of the spring constant of isotropic MREs increased rather linearly with increasing filler volume fraction (Fig. 25). With applied magnetic field the spring constants increased only when the filler fraction exceeded 15 vol.%. This further indicates that the interaction between the particles is possible when exceeding this filler fraction. The dynamic stiffness of isotropic MREs was also tuneable with the magnetic field when the filler fraction was between 17 and 25 vol.%. With a field strength of 0.13 Tesla the stiffness increased approximately by 5% from the zero-field value and with a field strength of 0.3 Tesla the increase was 10%. At higher filler volume fractions, the increasing magnetic field strength did not further increase the dynamic stiffness.
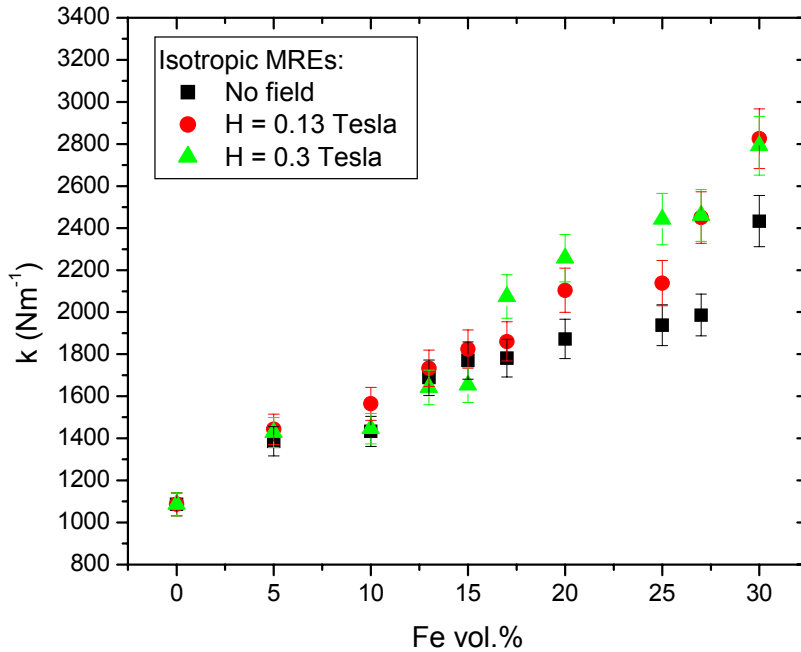
Figure 25. Measured average spring constant k *of isotropic MREs as a function of filler fraction. The spring constant is measured both without the magnetic field and with the field strength* H *values of 0.13 and 0.3 Tesla.*

When measured in Direction 1, the spring constant of aligned MREs was increasing markedly with the increasing filler fraction up to 27 vol.% of Fe (Fig. 26). When measured perpendicularly to the chains (Direction 2), the increase in the spring constant was much smaller and comparable to that of isotropic MREs. The values of the spring constant increased in both directions up to 25 vol.% of Fe and had maximum values between 25 and 27 vol.%. When applying the magnetic field, the values measured in Direction 2 increased with the filler volume fraction only at volume fraction values over 20 vol.%. In Direction 1 the values were increased due to the magnetic field for all the studied filler fractions. The relative increase due to the application of the magnetic field was also larger in Direction 1. When the filler fraction exceeds 10 vol.%, the dynamic stiffness of the aligned MRE composite is much higher when the load is applied parallel to the chains instead of perpendicular loading.

With the load applied in the chain direction the dynamic stiffness of aligned MRE increases with the increasing filler fraction up to 27 vol.% of Fe and

decreases slightly after that. This result is in agreement with the study by Davis [4], indicating that the particle interaction is strongest at this filler volume fraction. With applied magnetic field, the dynamic stiffness is tuneable with filler fractions exceeding 10 vol.%. Alignment of the particles allows the interaction between the particles to start with smaller filler fractions when measuring with the applied magnetic field. The reduced distance between the particles inside the chain can explain this behavior. However, in Direction 2 the interaction between the particles is much weaker; the effect of the magnetic field is noted only at filler fractions over 20 vol.% and it is comparable to that of isotropic MREs. The dynamic stiffness of the MREs is at highest when the load is applied in the chain direction and it can be further reinforced by the application of the magnetic field.
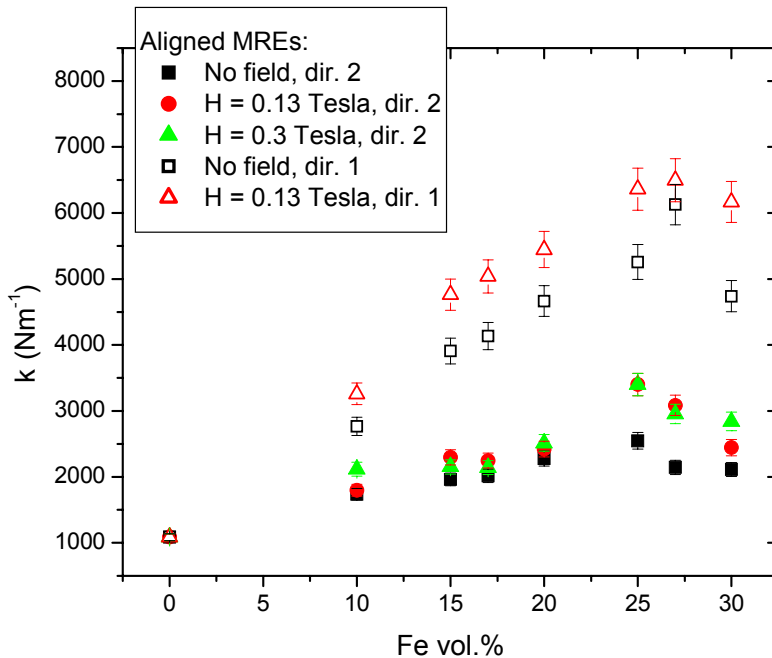

Figure 26. Average spring constant k *of aligned MREs as a function of the filler content when measured in Directions 1 and 2 (see Fig. 15). The spring constant is measured both without the magnetic field and with the field strength* H *values of 0.13 and 0.3 Tesla in Direction 2.*

11.2 Results of the DMA measurements at elevated temperatures

To study the influence of the magnetic field at elevated temperatures both aligned and isotropic MREs with 30 vol.% of Fe were characterized with the DMA. The DMA has a heating chamber where the measuring head with the sample can be placed. The silicones used in this study are applied for making moulds for the casting of low-melting metal alloys and they can be used up to temperatures of 300°C for short time periods. The unfilled silicone M4601 was used as a reference material in the tests. Frequency scans from 1 to 51 Hz were performed for each testing temperature in the temperature range from 20 to 130°C. The sample was placed in the 3-point bending fixture inside the heating chamber and the first scan was conducted at room temperature. After each frequency scan the heating chamber was programmed to increase the temperature to the next level, to stabilize the temperature and to restart the frequency scan for the same sample. To measure the samples in the magnetic field, permanent SmCo magnets were attached in the bending fixture inside the heating chamber. For each scan the values of the damping constant, damping ratio and spring constant were calculated as before. The aligned MREs were measured in Directions 2 and 3. In Dir. 3 the magnetic field is acting in the chain direction and in Dir. 2 perpendicular to the chains.

Figure 27 presents the measured damping constants of the MREs and unfilled silicone. In the figure it can be seen that at room temperature the application of the magnetic field increases the damping constant of the aligned MRE remarkably, when the magnetic field is applied in the chain direction. With increasing temperature, the damping constant increases up to 110°C when measured in Direction 3 under the influence of the magnetic field. When measured without the magnetic field in Direction 3, a peak is noted in the values of b in the temperature range of 40 to 60°C. At temperatures over 80°C, the passively measured values decrease to the same level as those measured at room temperature. In Direction 2 neither the magnetic field nor the increasing temperature has any notable influence on the damping constant. The increasing temperature in the whole measured temperature range does not influence the damping constants of unfilled silicone and isotropic MRE measured passively. However, in the magnetic field the damping constant of isotropic MRE increases linearly with increasing temperature.
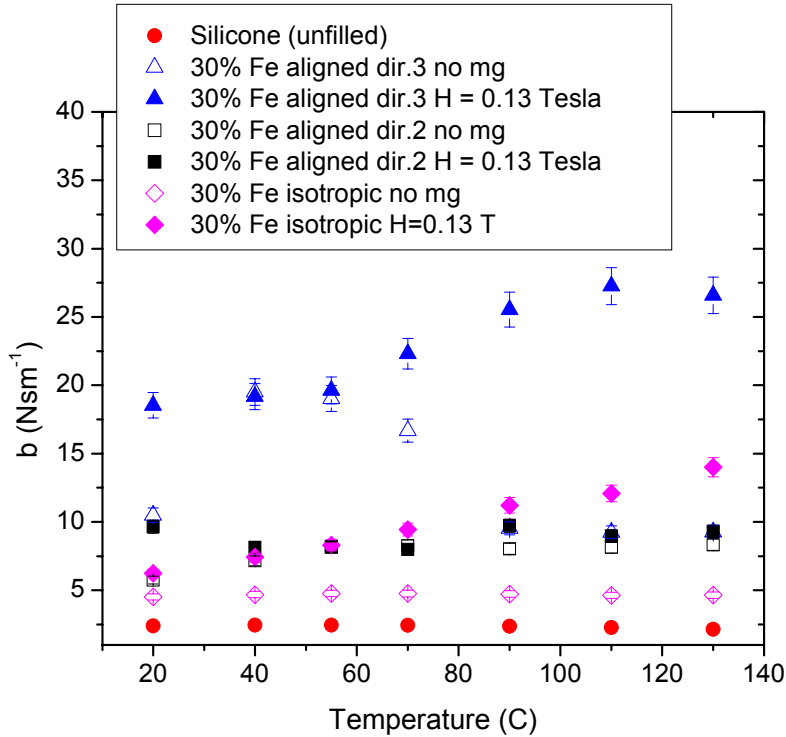
Figure 27. Damping constant b *as a function of temperature as measured for both isotropic and aligned MREs with 30 vol.% of Fe in Directions 2 and 3 (see Fig. 15) and for the unfilled elastomer M4601. The MREs are measured passively and with the magnetic field strength of 0.13 Tesla.*

Similar behavior can be seen in the damping ratio (Fig. 28). In Direction 3, the damping ratio of aligned MRE increases slightly with increasing temperature when measured with constant magnetic field strength. In Direction 2, an increase in damping is noted with increasing temperature when measured passively. With the magnetic field, the measured values show no tendency but behave in a rather random way. At higher temperatures (over 80°C) there is no difference between the values measured passively and with the magnetic field in Direction 2. The damping ratio measured for the unfilled silicone slightly decreases with the increasing temperature. The damping ratio of isotropic MRE measured also passively decreases slightly with increasing temperature at higher temperatures, but increases remarkably with the temperature in the magnetic field. For the isotropic MRE, the difference between the passively measured values of the

damping ratio and the values measured with the magnetic field increases remarkably with increasing temperature.
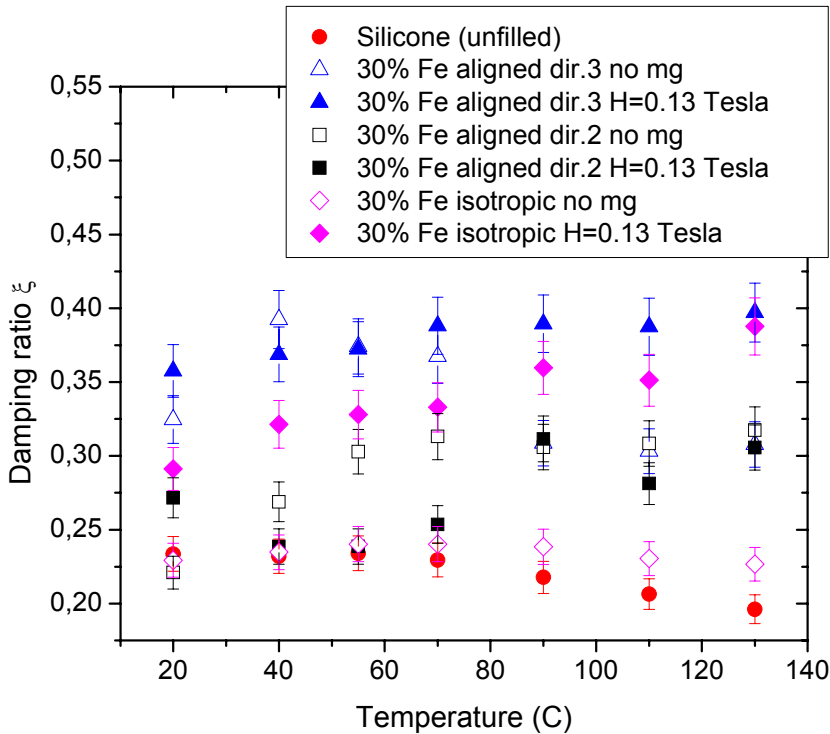

Figure 28. Damping ratio ξ as a function of temperature measured for isotropic and aligned MRE with 30 vol.% of Fe in Directions 2 and 3 (see Fig. 15) and for unfilled elastomer M4601. The MREs are measured both passively and with magnetic field strength of 0.13 Tesla.

The spring constant k measured at elevated temperatures shows similar behaviour. The increasing temperature does not influence the spring constant of either the unfilled silicone or the isotropic MRE in this temperature range. The spring constant of aligned MREs measured passively in Direction 2 decreases slightly with increasing temperature. In Direction 3 the spring constant of aligned MRE measured passively shows a peak in the temperature range of 40 to 60°C. However, the spring constant of the aligned MRE measured in Direction 3 with the magnetic field decreases initially slightly from the room temperature value with increasing temperature but stabilizes on a rather constant level at

temperatures over 80°C as can be seen in Fig. 29. In Direction 2, the spring constant values are not increasing due to the application of the magnetic field. The spring constant of isotropic MRE increases slightly with increasing temperature when measured in the magnetic field.
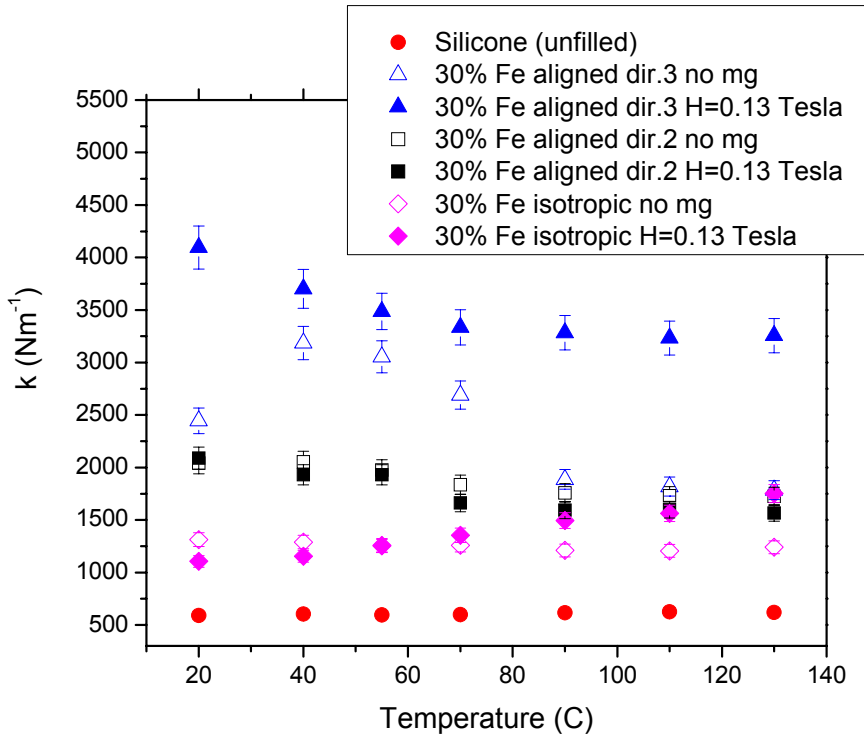

Figure 29. Spring constant k as a function of temperature measured for both isotropic and aligned MREs with 30 vol.% of Fe in Directions 2 and 3 (see Fig. 15) and for unfilled elastomer M4601. The MREs are measured both passively and with the magnetic field strength of 0.13 Tesla.

The aligned MREs measured without the magnetic field showed a small increase of stiffness and damping with increasing temperature at temperatures between 40 and 60°C when measured in Direction 3 but the values decreased notably at temperatures above that temperature range. This decrease in stiffness and in the corresponding peak value of damping could indicate that the T_g of the elastomer shell surrounding the particles is exceeded in this temperature range. The decrease in stiffness is also visible when measured with the applied magnetic

field in the same temperature range. With the applied magnetic field and increasing temperature the spring constants decreased slightly up to 70°C and stayed on a constant level after that with increasing temperature.

Isotropic MREs and aligned MREs measured in Direction 2 did not behave similarly. The aligned MREs measured in Direction 2 were only slightly influenced by the increasing magnetic field or temperature. In isotropic MREs the changes were more pronounced, especially with increasing temperature. The particles in isotropic MREs were able to move more freely with increasing temperature, which increased the stiffness moderately and damping ratio remarkably. The energy dissipation by the isotropic system in magnetic field was clearly enhanced with increasing temperature. As compared with isotropic MREs, the increasing temperature did not render similar extra particle mobility to aligned MREs. The directionality of the aligned MREs was observed here as well; when measured with magnetic field in Direction 3 (see Fig. 15: magnetic field applied in the chain direction) the spring constant was increased markedly at low temperatures. Increasing temperature did not have any notable influence on stiffness when the same material was measured in Direction 2. The stiffness of the unfilled silicone used as a reference material did not react to the increasing temperature in the studied temperature range. The damping ratio of the unfilled silicone was slightly decreasing with increasing temperature.

11.3 Results of the static and dynamic compression testing

In this chapter the results obtained from the compression testing of spring elements consisting of aligned and isotropic MREs with 30 vol.% of Fe and of unfilled silicone are discussed. In these measurements, two different coil devices were used. In Coil 1 the magnetic field is uniform across the MRE sample which is not the situation with Coil 2. In Coil 1 the increasing magnetic field strength adds some prestress on the sample, while in Coil 2 the prestress is purely mechanical. Due to these factors the results shown here are connected to the coil device with which they have been measured.

11.3.1 Static compression

The static stress response in compression was measured for the aligned MRE spring elements as a function of the magnetic field strength. The Instron machine was used for measuring the response of the MRE spring elements located inside the coil device. The dimensions of the cylindrical spring elements were as follows: diameter 50 mm and height 20 mm. The stress-strain curves for the aligned MRE with 30 vol.% of Fe were measured with increasing magnetic field strength in the coil device 2. The compressive load and the magnetic field were applied in the chain direction of the MRE element. In these tests, the maximum compressive strain of 6.5% was used and the corresponding loading force was recorded. Figure 30 shows that the static stress corresponding to a definite strain increases with increasing magnetic field strength.
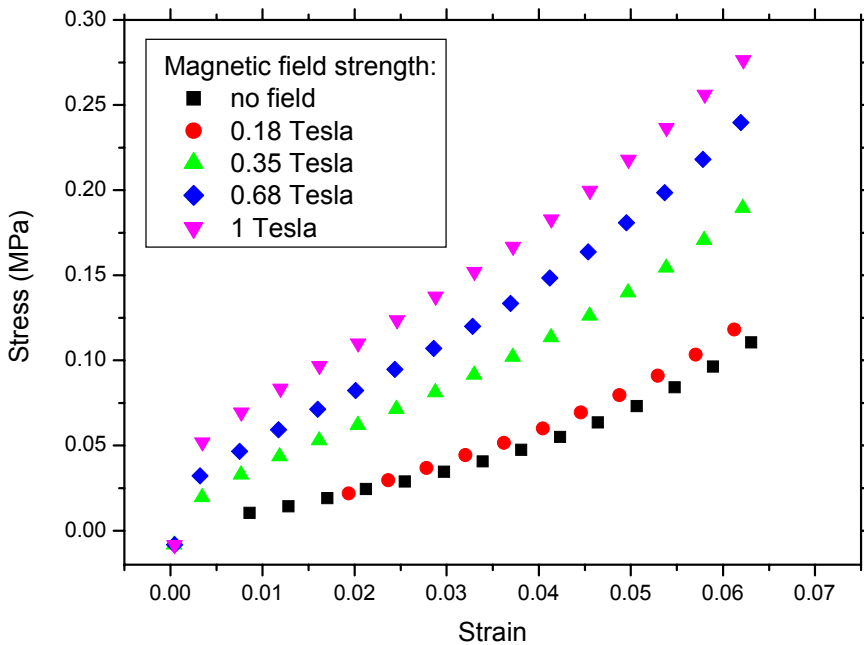

Figure 30. Stress-strain curves measured in compression with Coil device 2 at room temperature for the aligned MRE with 30 vol.% of Fe in the direction of chains and with different magnetic field strength values.

The compressive elastic modulus (E) values were calculated from the slope of the force-displacement measurements using the strain range up to 0.02. In Fig. 31 the elastic modulus of aligned MRE is presented as a function of the magnetic field strength inside the coil. The values of elastic modulus increase rather linearly with the magnetic field strength at small and moderate field strength values. At the field strength H value of about 0.8 Tesla the saturation of Fe particles in the MRE changes the linear behaviour. At saturation ($H \sim 1$ Tesla), the value of the elastic modulus was twice as large as the zero field value of the MRE.
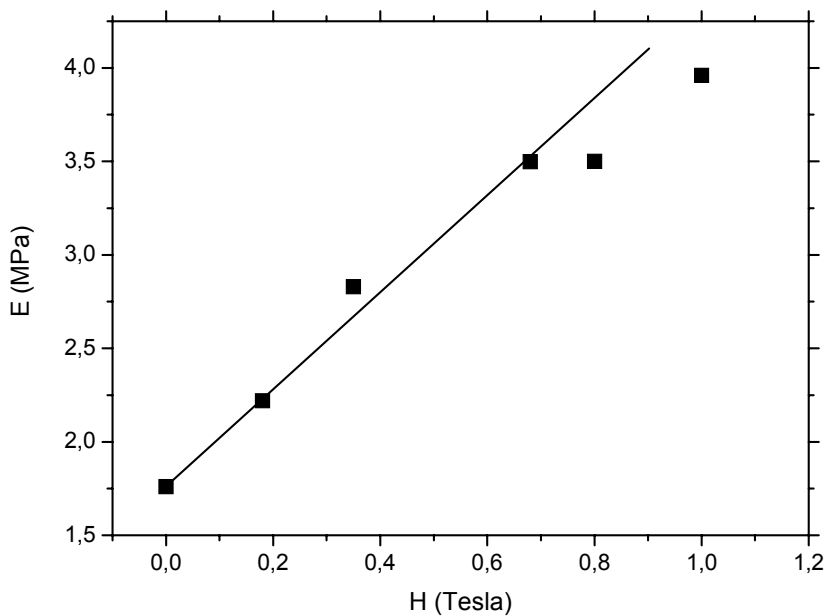
Figure 31. Room temperature elastic modulus E of an aligned MRE with 30 vol.% of Fe as a function of magnetic field strength H. The modulus is measured and the magnetic field is applied in the direction of chains.

11.3.2 Dynamic compression

Aligned MREs with 30 vol.% of Fe were characterized in dynamic compression. In dynamic compression, the compressive load and the magnetic field were applied in the direction of the particle chains. In dynamic testing the

displacement amplitude was first kept constant at ± 5% and the excitation frequency was varied from 0.5 to 15 Hz. For comparative purposes, the isotropic MRE with 30 vol.% of Fe was characterized at the frequency of 10 Hz both without the magnetic field and with the magnetic field strength H of 0.35 Tesla with Coil device 1. The mechanical prestress subjected on the sample was 0.2 kN, which was increased by the magnetic attractive force on the cover. This force increased the load on the sample. The magnitude of the magnetic load depended on the strength of the magnetic field, the permeability of the sample and on the strain amplitude and was therefore difficult to measure. For this reason, the magnetic field strength used in Coil 1 was restricted to 0.35 Tesla. The same mechanical prestress of 0.2 kN was used in the measurements with Coil 2.

By determining the energy loss per cycle from several ($n \sim$ 40–50) consecutive force-displacement loops measured with constant magnetic field strength at a definite frequency, the dynamic stiffness and loss factor were calculated using the Equation (34). The slope of the major axis of the force-displacement loop (and consequently the dynamic stiffness) increased when the magnetic field strength H was increased in the coil as can be seen in Fig. 32, where the testing frequency was 1 Hz. In addition, the surface area of the hysteresis loop increased with increasing field strength indicating that the dynamic loss factor increased with the magnetic field strength.
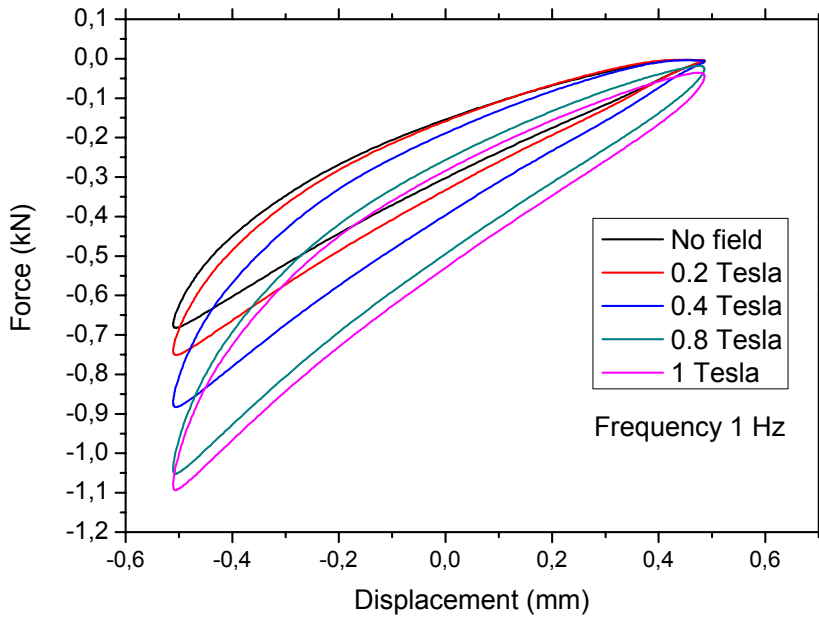
Figure 32. Measured force-displacement loops with different magnetic field strength values for the aligned MRE with 30 vol.% of Fe, when studied with the applied load and magnetic field in the direction of chains in Coil device 2 with testing frequency of 1 Hz.

The average increase of the dynamic stiffness of aligned MRE with 30 vol.% of Fe was 10.9% when the field strength H was increased from 0 to 0.35 Tesla in Coil 1 and the corresponding average increase of the loss factor was 18.5%, respectively. The average value changes for each testing frequency measured in Coil 1 are given in Table 5.

Table 5. Average changes (in %) of the spring constant and loss factor values of an aligned MRE as measured in the direction of chains at different frequencies, when the magnetic field strength H is increased from 0 to 0.35 Tesla in Coil 1. The isotropic MRE is measured at 10 Hz with H = 0.35 Tesla.

Material	Aligned MRE 30%					Isotropic MRE 30%
Frequency (Hz)	0.5	1	5	10	15	10
Increase in spring constant (%)	10.0	11.2	11.4	11.2	12.2	11.0
Increase in loss factor (%)	30.6	30.5	16.6	8.0	13.3	11.7

The curves for the spring constants and the loss factors of an aligned MRE as a function of testing frequency are presented in Figs 33 and 34. The spring constant k indicates the elastic energy stored and recovered by the system. In Fig. 33 it can be seen that the dynamic stiffness increases proportionally with the applied field strength in the studied frequency range. The passively measured dynamic stiffness increases also with increasing frequency, which is typical for most elastomers [18, 46]. As shown in Fig. 34, the loss factor generally increases with the applied field strength at each testing frequency level, but the increment depends on the testing frequency. At low frequencies the values of loss factor are generally higher and they decrease with increasing frequency. The loss factor is defined as the ratio of the loss and storage moduli values as described by Equation (13). When the dynamic stiffness increases with increasing frequency, the storage modulus also increases. The measured values of loss factor decrease with increasing frequency, indicating that the loss modulus is not significantly influenced by the increasing frequency in this frequency range.
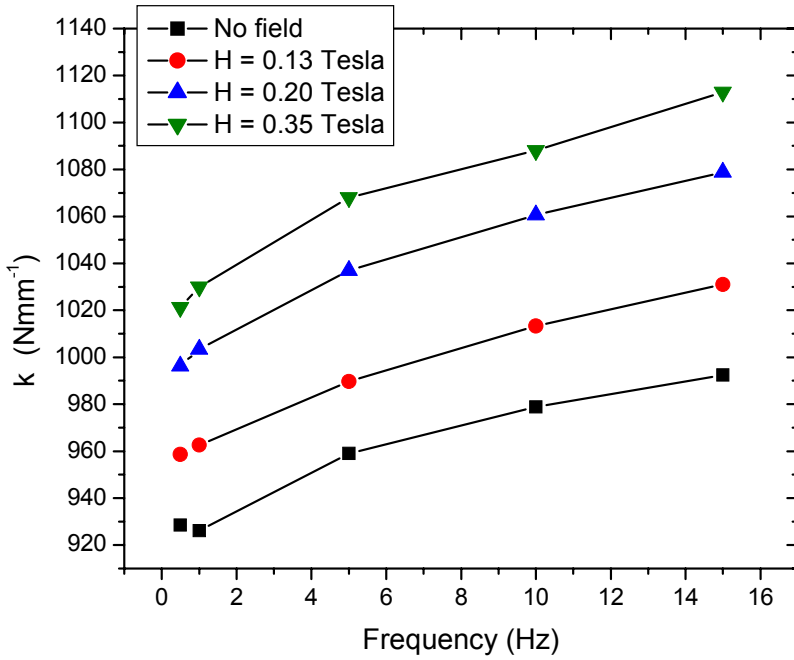
Figure 33. Spring constant k *of an aligned MRE with 30 vol.% Fe as a function of the testing frequency, when measured in the direction of chains with different magnetic field strength values in Coil 1. The magnetic field is applied in the direction of chains.*
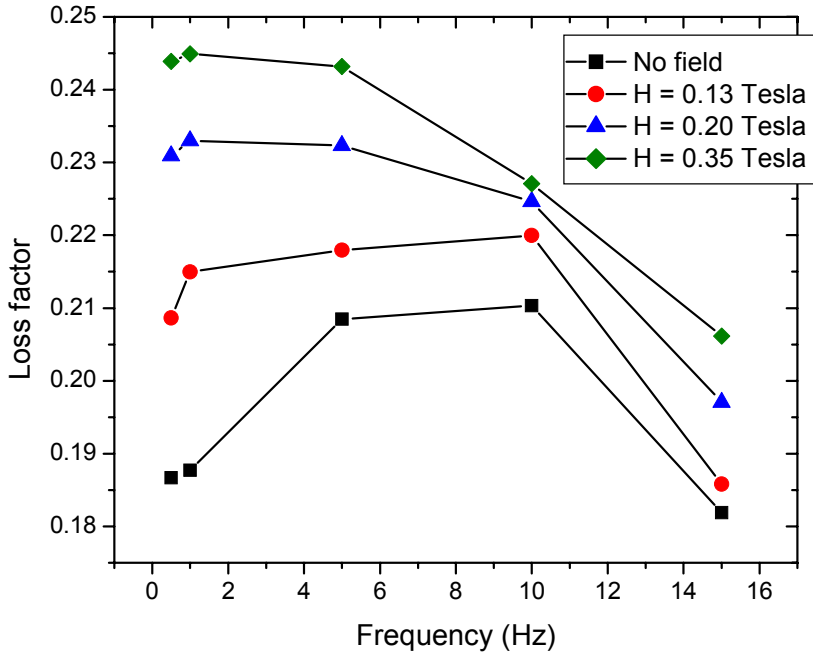
Figure 34. Loss factor of an aligned MRE with 30 vol.% Fe as a function of the testing frequency, when measured in the direction of chains with different magnetic field strength values in Coil 1. The magnetic field is applied in the direction of chains.

Next the MRE spring elements were studied with different strain amplitudes by keeping the testing frequency constant at 1 Hz. In addition to the aligned and isotropic samples, an unfilled silicone sample was studied. The measurements with magnetic field were carried out with higher field strength values to maximize the MR effect. The coil current of 16 A was used, and the field strength *H* measured inside the Coil 1 was 0.87 Tesla for the aligned MRE, 0.77 Tesla for the isotropic MRE and 0.46 Tesla for the unfilled silicone sample.

The compressive stiffness of the samples is presented in Fig. 35. The dynamic compressive stiffness of the unfilled silicone does not depend on the strain amplitude and it is not influenced by the magnetic field. The isotropic MRE has initially higher stiffness than the unfilled silicone and the stiffness is only slightly influenced by the strain amplitude. Furthermore, the applied magnetic field does not increase the compressive stiffness of the spring elements consisting of isotropic MREs in Coil 1. This is probably due to the increased

magnetic prestress. The spring element with aligned MRE has initially a very high stiffness as compared to the isotropic MRE and the stiffness measured without magnetic field decreases with increasing strain amplitude. The magnetic field increases the stiffness of the aligned MRE at all measured strain amplitudes. The increase is initially 10%, but it decreases constantly with increasing strain amplitude so that with a strain amplitude of 10% the increase in stiffness is only 3%. The decrease in dynamic stiffness with increasing strain amplitude is due to the Payne effect, indicating that the strain amplitude affects the structure of particle network. The particle network can be reinforced with applied magnetic field.
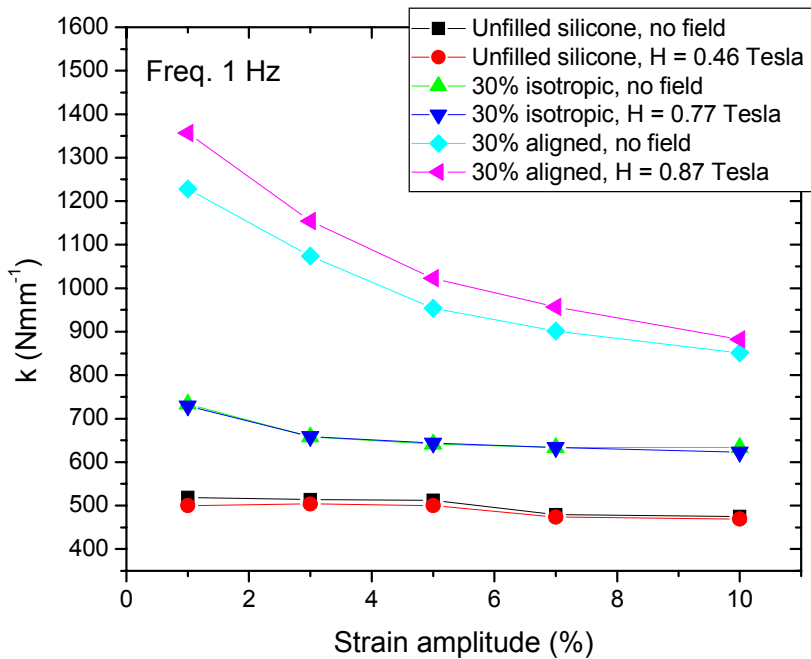
Figure 35. Spring constant k *of an unfilled silicone (M4644) as well as of the isotropic and aligned MREs with 30 vol.% of Fe as a function of the strain amplitude when measured in Coil 1 both without and with the magnetic field using the frequency of 1 Hz. The magnetic field is applied in the chain direction.*

For comparative purposes, the aligned and isotropic MREs with 30 vol.% Fe were also measured in Coil 2 with the magnetic field strength ranging from zero to approximately 1 Tesla. Figure 36 shows the dynamic stiffness (spring

constant *k*) of the aligned MRE with 30 vol.% of Fe as a function of the magnetic field strength when measured with Coil 2 at the frequency of 1 Hz and with compressive strain amplitude of 2.5% and 5%. At a compressive strain amplitude of 5% the dynamic stiffness is increased rather steeply with the magnetic field strength up to the value of 0.8 Tesla.
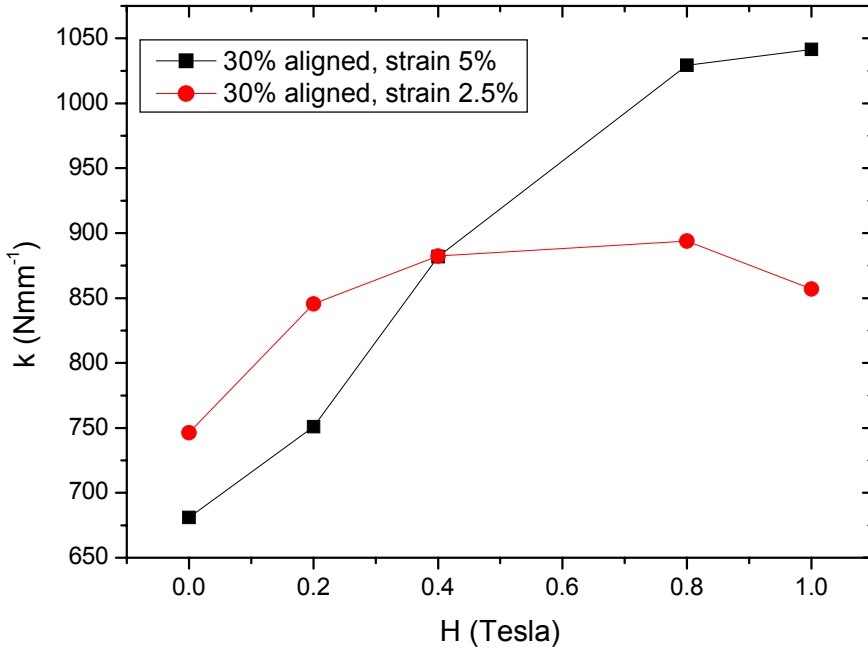
Figure 36. Spring constant k *of the aligned MRE with 30 vol.% Fe when measured as a function of the magnetic field strength* H *inside Coil 2, at the frequency of 1 Hz with 2.5% and 5% compressive strain amplitudes.*

The loss factor values of aligned MRE spring elements are also slightly influenced by the strain amplitude as can be seen in Fig. 37. In magnetic field, the loss factor values increase slightly from the zero-field values up to the field strength values of about 0.4 Tesla. The slight increase in damping with the increasing magnetic field strength was also noticed in the DMA measurements in Direction 2. At magnetic field strength values exceeding 0.4 Tesla, the loss factor values decrease slightly when the strain is 5%. The slightly decreasing damping with increasing magnetic field strength was also found in reference [10], where an aligned MRE was characterized in free vibration with dynamic compressive load.

Figure 37. Loss factor of aligned MRE with 30 vol.% of Fe as a function of the magnetic field strength H, when measured in Coil 2 at the frequency of 1 Hz with 2.5% and 5% compressive strain amplitudes. The magnetic field is applied in the direction of chains.

The dynamic stiffness and loss factor values of isotropic MREs with 30 vol.% of Fe were also measured at magnetic field strength values higher than 0.5 Tesla (see table 5). Figure 38 compares the spring constants of isotropic and aligned MREs measured with 2.5% strain amplitude. The change in the spring constant of isotropic MRE with increasing magnetic field strength is very small as compared to that of the aligned MRE. This is due to the lack of the chain-like particle structure, which can resist the compression.

Figure 38. Comparison of the spring constant k *of isotropic and aligned MREs with 30 vol.% of Fe as a function of the magnetic field strength when measured at the frequency of 1 Hz and with the strain amplitude of 2.5% in Coil 2. The magnetic field is applied in the direction of chains.*

The measured loss factor values of isotropic and aligned MREs are compared in Fig. 39. The figure shows that the loss factor of aligned MRE spring element does not change much with increasing magnetic field strength. The loss factor increases initially slightly but stabilizes at the value of about 0.2 Tesla. However, the loss factor of the isotropic MRE spring element in magnetic field is increased with increasing magnetic field strength up to the field strength of 0.8 Tesla.
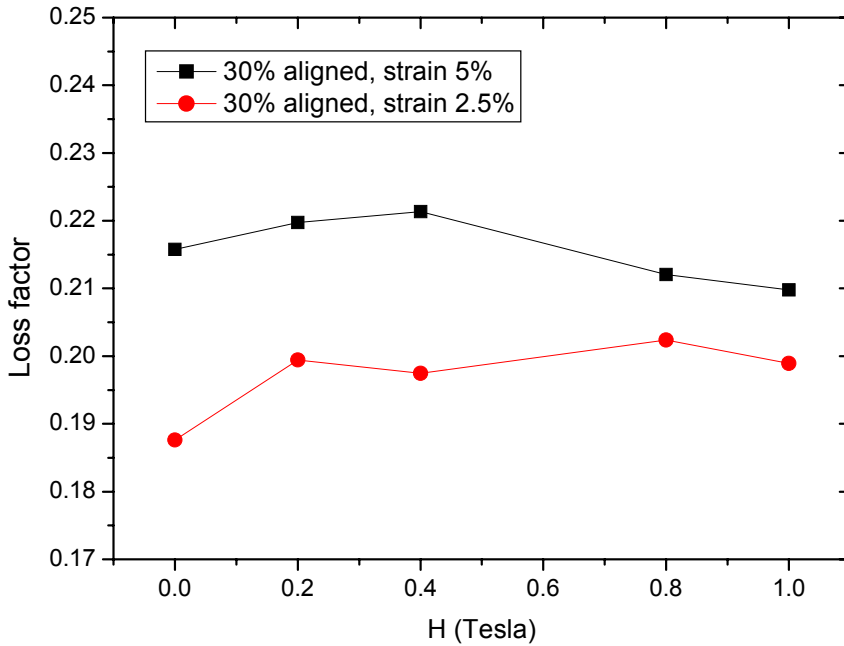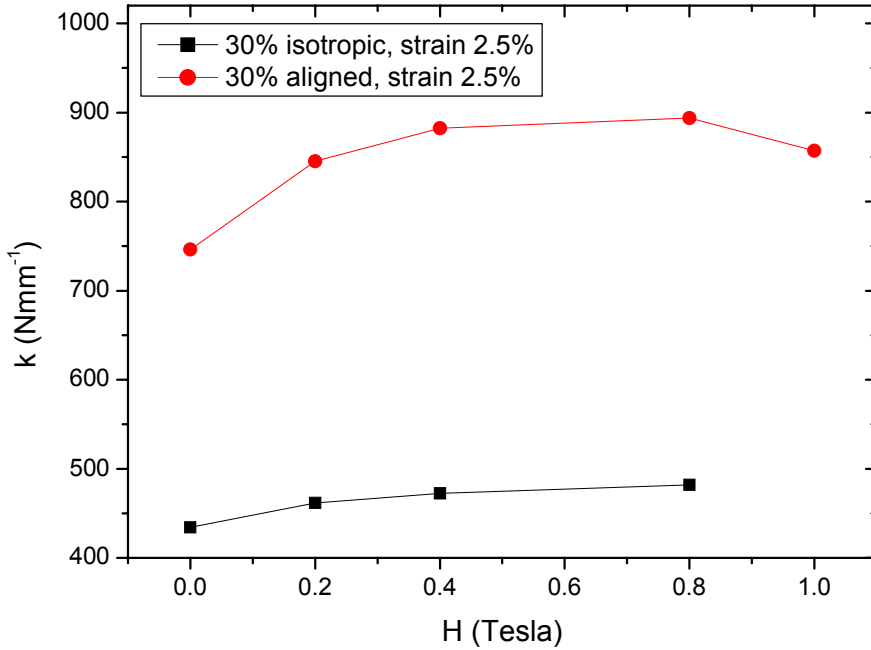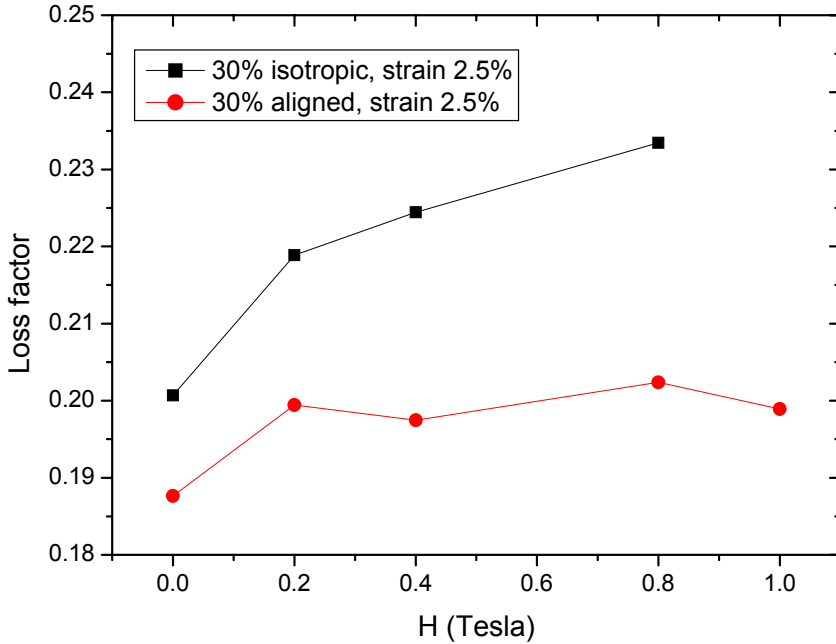
Figure 39. Comparison of the loss factor values of isotropic and aligned MREs with 30 vol.% of Fe as a function of the magnetic field strength when measured at the frequency of 1 Hz and with the strain amplitude of 2.5% in Coil 2. The magnetic field is applied in the direction of chains.

Zhou [12] has measured the damping ratio in free vibration for aligned silicone MRE with 27 vol.% of Fe when the magnetic field and the external load causing the free vibration were applied in the direction of chains. The measured value in resonance at saturation was 0.24, which is nearly the same (0.23) as measured for aligned silicone MREs with 27 vol.% of Fe in Direction 2 with the magnetic field strength of 0.13 Tesla in this study. He also stated that the zero-field value of the damping ratio of their vibration system is the same (0.24) as that measured with magnetic field at saturation. Increasing the magnetic field strength over 1 Tesla had almost no effect on the damping ratio; its value was decreasing only by about 10%.

It seems that the different results on the damping characteristics of the MREs obtained in various studies are due to the strongly directional damping behaviour of this composite material. In aligned MREs measured in the chain direction the increase in damping in magnetic field is very small and has no practical

significance. In the perpendicular direction, the increase in damping is higher in moderate magnetic field as shown by the results of the DMA measurements. The damping of the MREs is tuneable in the magnetic field when the deformation in dynamic loading is not located in aligned particle chains. The dynamic stiffness of aligned MREs is also tuneable in the magnetic field under compressive loading, which allows the design of magnetically controllable spring elements based on these materials.

12. Measurement of the elastic properties of the MREs

In this chapter, the elastic properties of isotropic MREs are studied and compared with the existing models of isotropic composite materials. The elastic properties of isotropic and aligned elastomers are also compared to reveal the reasons for the different behaviour of these composites.

12.1 Ultrasonic measurements of the bulk modulus (K)

The pulse-echo technique was used for measuring the longitudinal modulus c_{11} of the MREs. The longitudinal modulus was measured using the RF technique for sending longitudinal sound waves into the material. The echoes were recorded and the longitudinal sound velocity in the material was calculated. The pulsed longitudinal RF waves with about 1 MHz frequency were transmitted to the MREs by a contact transducer V103-RM (Panametrics, Inc.) and Ritec Advanced Measurement System RAM-10000 recorded the echoes. To ensure the contact, silicon oil was used between the MRE surface and the transducer.

The longitudinal wave is in our case a compressional wave where the particle motion is parallel to the propagation direction of the wave. The sound velocity in the material is calculated from the time of flight between the echoes. The longitudinal modulus c_{11} can be consequently calculated from the sound velocity by using Equation 36 [21, 23]:

$$c_{11} = \lambda + 2\,G = \rho\,\upsilon^2 \tag{36}$$

where λ is the Lame constant, G is the shear modulus, ρ is the density and υ the longitudinal sound velocity of the material [21]. The measured c_{11} values for isotropic and some aligned MREs are presented in Fig. 40. The c_{11} of aligned MREs was measured parallel to the particle chains (Direction 1, see Fig. 15). Figure 40 shows that in isotropic MREs the longitudinal modulus increases with the increasing volume fraction of filler from the value of 9 GPa for pure silicone to 24 GPa for the isotropic MRE with 30 vol.% of Fe. For the aligned MREs the

longitudinal modulus in the chain direction is much higher than that of the isotropic MREs with the same filler content.
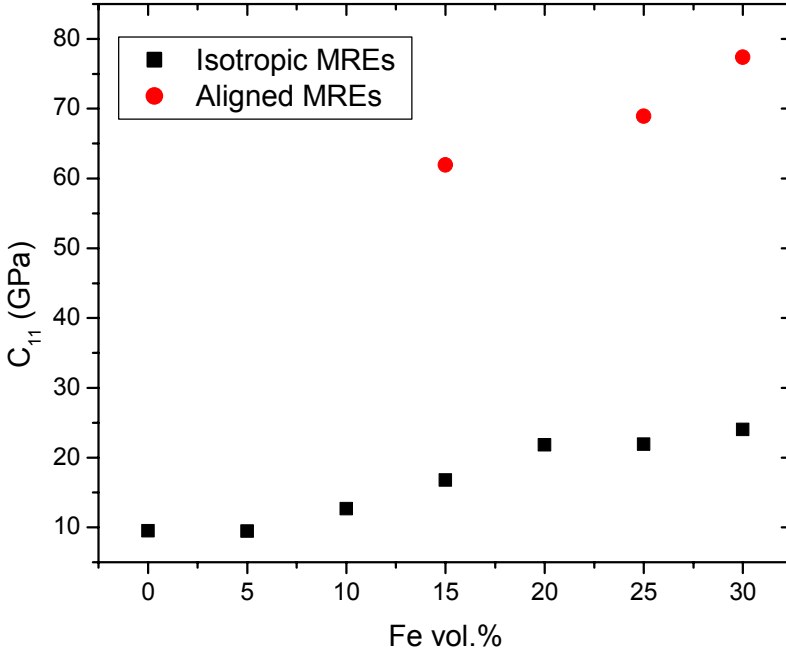
Figure 40. Longitudinal modulus c_{11} *of isotropic and aligned MREs as a function of filler content when measured without the magnetic field.*

The bulk modulus K values of isotropic MREs were calculated from the measured values of the longitudinal modulus c_{11}. These are related according to the Equation (37) [21].

$$K = \lambda + \frac{2G}{3} = c_{11} - \frac{4}{3}G \qquad (37)$$

On the basis of Equation (37), the bulk modulus of isotropic MREs has practically the same value as the longitudinal modulus due to the great difference in magnitude between the shear modulus G and c_{11} values. For a perfectly elastic solid, or for a viscoelastic solid in equilibrium, the equilibrium Young's modulus is related to the shear and bulk modulus values as follows [3]:

$$E = \frac{G(3\lambda + 2G)}{\lambda + G} = \frac{9GK}{G + 3K} = 2G(1 + \nu) \tag{38}$$

where ν is the Poisson's ratio. As both G and K are time-dependent, the $E(t)$ must be specified in terms of G and Poisson's ratio ν by integrating over the time range. In soft elastic solids like silicone elastomers the $K(t)$ is often larger than $G(t)$ by two orders of magnitude or more in definite broad ranges of time. This situation corresponds to the Poisson's ratio ν value very close to 0.5. In this case, the time-dependence of ν can be ignored and Equation (38) can be reduced to a following form [18]:

$$E = 3G(t) \tag{39}$$

This equation applies to polymers characterized with for example extension tensile test or shear. However, the use of Equation (39) is limited; not only to materials with Poisson's ratio ν very close to 0.5 but also to small deformations and small deformation rates [18].

12.2 Elastic modulus values of isotropic MREs

The values of the elastic or Young's modulus of isotropic MREs were calculated using the Rayleigh's method on the data obtained from the DMA 3-point bending measurements of the MRE samples with different filler contents. When applying an oscillating force F_0 the rectangular sample has the maximum deflection z_0 as compared to the static situation:

$$z_0 = \frac{F_0}{4 E w_s} \left(\frac{L_s}{h_s} \right)^3 \tag{40}$$

where w_s is the sample width, L_s is the sample length, h_s is the sample height and E is the Young's modulus. The maximum deflection is very small, ranging from 0.01 mm to about 0.1 mm in resonance (Figures 18 and 19). As the weight of the sample is small in comparison with the system mass, it can be assumed that the deflection curve of the rectangular sample during vibration has the same shape as the static deflection curve caused by the same force [20]. The spring constant

k denotes the force required to produce a unit change in the length of the sample. The deflection caused by the static force F_0 is $z_0 = F_0 / k$ and the Young's modulus can be defined as:

$$E = \frac{k}{4 w_s} \left(\frac{L_s}{h_s} \right)^3 \tag{41}$$

The results of the calculations of Young's modulus of isotropic MREs are presented in Fig. 41. The elastic modulus increases monotonically with increasing filler content from the value of 1.2 MPa of unfilled silicone to about 2.7 MPa measured for MRE with 30 vol.% of iron. When applying magnetic field, no systematic change in E is observed with filler contents below 15 vol.% of Fe. At 27 vol.% of Fe, the maximum increase of elastic modulus in magnetic field is about 0.5 MPa. Increasing the field strength from 0.13 to 0.3 Tesla has a small influence on the elastic modulus only at filler fractions ranging from 17 to 25 vol.%.
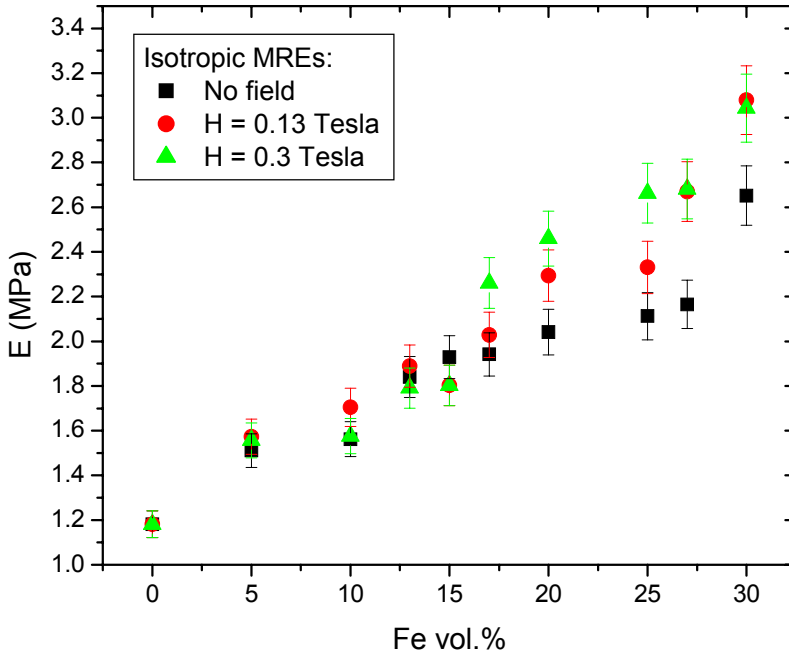

Figure 41. Young's modulus E *of isotropic MREs as a function of the filler content when measured both without external magnetic field and with field strength values of 0.13 and 0.3 Tesla.*

The shear modulus calculated with Eq. (38) values for isotropic MREs as determined without magnetic field and with the field strength H values of 0.13 and 0.3 Tesla are presented in Fig. 42 as a function of the filler content. Without magnetic field, the shear modulus increases with increasing filler fraction from the initial value of 0.4 MPa for unfilled silicone to about 0.9 MPa for MRE with 30 vol.% of iron. With applied magnetic field, the shear modulus starts to increase with filler content when the filler volume fraction is larger than 15%. The maximum increase of shear modulus due to the application of the magnetic field is about 10% at the filler fractions of 25 to 27 vol.%.

A few models have been developed for predicting the increase in shear modulus with the increasing filler fraction of the filled polymer composites. Davis [4] has used the Equation (3) by Guth [32] for predicting the shear modulus G_{ran} of rubber filled with randomly dispersed, rigid particles. The equation has two parameters: G_0 is the shear modulus of the unfilled rubber and ϕ is the volume fraction of filler particles. The equation was first developed for predicting the influence of carbon black filler on the shear modulus of rubber and it is based on the hydrodynamic theory. The values predicted by this equation in our case are presented also in Fig. 42.

Christensen [19] has developed general models for the elasticity of heterogeneous isotropic composite materials. In the determination of the effective stiffness properties (the average stiffness of the composite) the properties and interaction of all the phases of the heterogeneous media are taken into account. The three-phase model describes the situation where rigid spherical inclusions are embedded in a continuous matrix. In the current work the experimental data on shear modulus was compared to the values predicted by the non-dilute case of the three-phase model by Christensen. The material parameters used in the calculation of the non-dilute model values are presented in Table 6. The formulas used for calculation can be found in ref. [19]. A Fortran-based program was used for calculation and the calculated values are presented in Fig. 42.

Table 6. The material parameters used in the calculation of shear moduli values with the non-dilute model of Christensen [19].

Shear modulus of the inclusions	80 GPa
Shear modulus of the matrix	0.004 GPa
Bulk modulus of the inclusions	200 GPa
Bulk modulus of the matrix	9 GPa
Poisson's ratio of the inclusions	0.35
Poisson's ratio of the matrix	0.5

Christensen has also developed a model for a concentrated suspension, where the packing arrangement of the particles is specified and taken into account [19]. In concentrated suspension model the packing arrangement is thought to be a loosely packed cubical structure. Similarly to the model of Guth [32], this model depends only on the volume fraction ϕ of the rigid particles and on the shear modulus G_0 of the matrix as shown in Equation (5). This model is only valid up to the maximum volume fraction for cubical packing, which is $\phi_{max} = \pi/6$. The shear modulus values predicted by the concentrated suspension model of Christensen are also presented in Fig. 42.
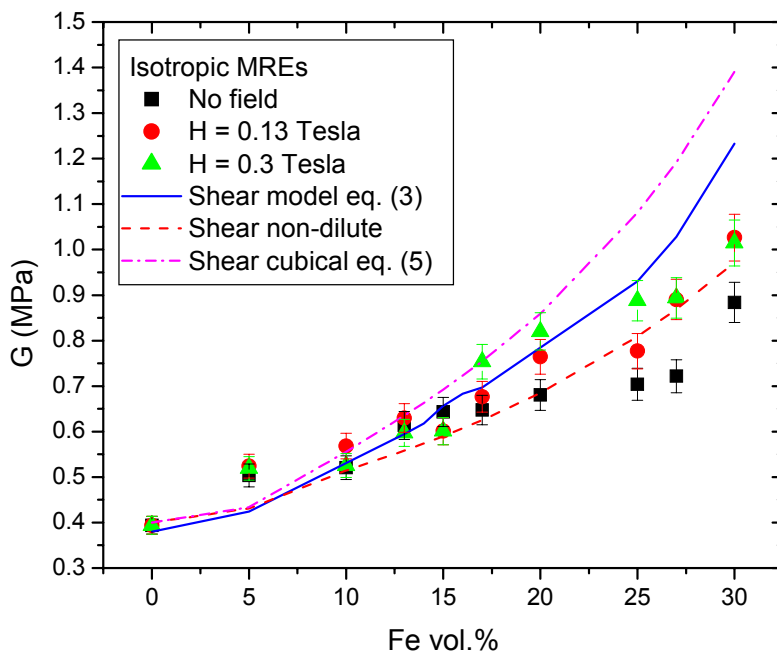
Figure 42. Calculated values of the shear modulus G *of isotropic MREs as a function of filler content when the DMA measurements were carried out both without external magnetic field and with the magnetic field strength* H *values of 0.13 and 0.3 Tesla. Experimental results are compared to the values predicted by Equation (3) and to the values suggested by the non-dilute and concentrated suspension models (Eq. (5)) by Christensen [19].*

The values predicted by Equation (3) and the concentrated suspension model (Eq. (5)) correspond to the measured shear modulus data up to the filler fractions of about 15 vol.%. At filler fractions over 15 vol.%, both models suggest that the value of shear modulus should increase more rapidly with the increasing filler content than what the measured values actually do. The non-dilute model has quite a good correspondence with the experimental values in the whole range of 0 to 30 vol.%. This result reveals that the filler particles in the isotropic MREs are homogenously distributed in nondilute suspension.

12.3 Elastic modulus values of aligned MREs

Differently from the isotropic MREs, the elastic moduli values of aligned MREs depend on the measurement direction. The Young's modulus E was calculated using the Rayleigh's method and the results from the DMA measurements both in the direction of the particle chains and perpendicular to them (Directions 1 and 2 in Fig. 15). The calculated values are presented in Fig. 43. When measured without the magnetic field in the direction parallel to the chains (Direction 1 in Fig. 15), E increases first with increasing filler fraction from the initial value of 1.2 MPa of the unfilled silicone to about 2.5 MPa of the MRE with 17 vol.% of iron but remains then at a quite constant level between 17 and 30 vol.%. When applying the magnetic field, a small overall increase in E values is observed between 25 to 30 vol.% of Fe. The maximum change is about 0.5 MPa. When measured perpendicular to the chains (Direction 2) without field, the E values increase steeply up to 20 vol.% and decrease after that. The maximum value of 3.7 MPa is found at 20 vol.%. With the applied magnetic field, a small increase is noted in the measured values at filler fractions over 20 vol.%. The maximum increase of 1.3 MPa occurs at 27 to 30 vol.% of Fe.

Aligned MREs are often modeled as materials with a cubical lattice structure. This assumption is based on the studies concerning MR fluids, where the particles can be arranged quite freely along the magnetic field lines with corresponding particle packing. From the cubical symmetry it follows that the values of Young's modulus measured in three directions perpendicular to each other should be in the same range. In this study, the measured values of E have a remarkable difference at filler fractions over 15 vol.% when measured in parallel and perpendicular directions to the particle chains in aligned MREs. The evident conclusion is that with filler fractions over 15 vol.% the aligned chain-like structure has no cubical symmetry. Therefore, when the dynamic bending is carried out so that the bending axis is in the direction of the chains, the measured Young's moduli are considerably higher than in the direction perpendicular to the chains. Also, the values of shear and longitudinal moduli should then be different in both directions.
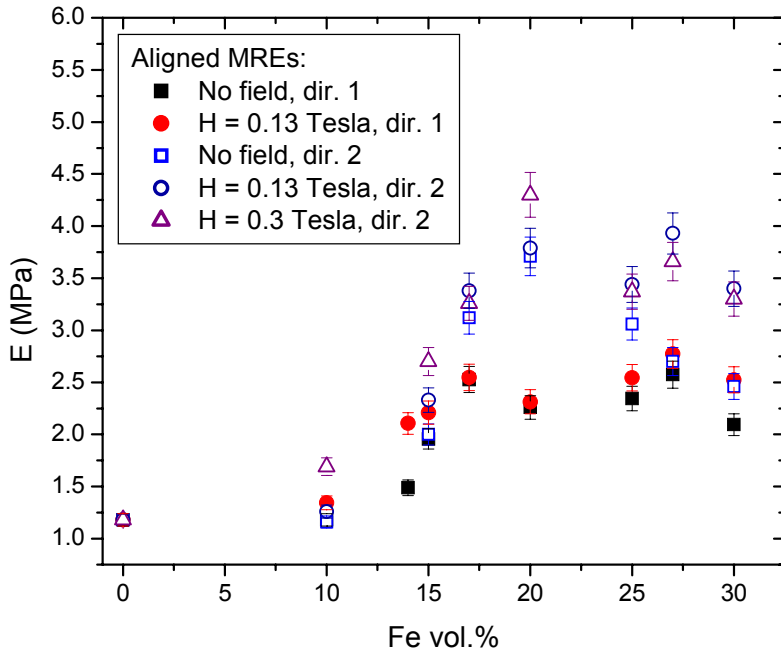
Figure 43. Young's modulus E *of aligned MREs as a function of the filler content when measured in Directions 1 and 2 (see Fig. 15) both without the magnetic field and with the field strength* H *values of 0.13 and 0.3 Tesla.*

13. Magnetization of the MREs

The magnetization of the isotropic MREs was measured using the superconducting quantum interference device (SQUID). The SQUID magnetometer is very sensitive and can be used to detect very small magnetic signals also in living organisms. It uses a liquid helium cooled amplifier to measure the magnetic moment in the range of 10^{-7} to 300 emu with varying magnetic field. The weights of the MRE samples were 0.024, 0.020 and 0.018 g for the MREs containing 15, 20 and 30 vol.% of Fe, respectively. The saturation magnetization M_s of bulk iron is 220 emu/g. From the measured magnetization curves (Fig. 44) it can be seen, that the saturation magnetization of the MREs increases with the increasing volume fractiont of iron. The saturation starts in all cases at the same magnetic field strength.

For the samples containing 30 vol.% of Fe particles (75 weight % Fe), the saturation magnetization is 160 emu/g, which is close to the expected value of 0.75 x 220 emu/g. Independent on the filler fraction, the saturation of the MREs occurs when the applied field strength is about 1 Tesla. The saturation can be seen to start at the field strength of about 0.7 Tesla.
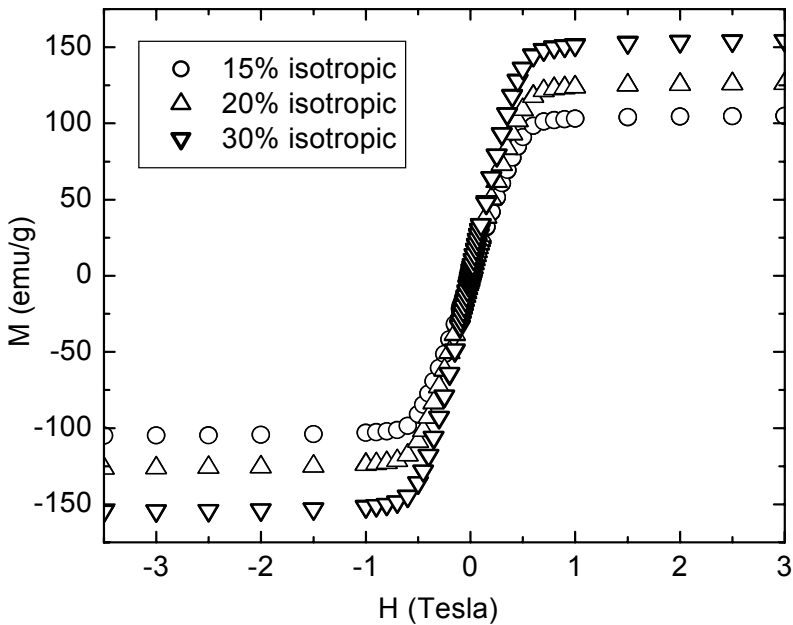

Figure 44. Magnetization curves measured with the SQUID for the isotropic MREs with 15, 20 and 30 vol.% of Fe.

14. Discussion

In the following, the elastic and vibration damping properties of isotropic and aligned MREs are discussed in the light of the results obtained from the measurements carried out in this study.

14.1 Influence of particle arrangement on the properties of the studied MREs

Magnetorheological elastomers are "smart" composites, whose viscoelastic properties can be controlled by applying an external magnetic field. The mechanical properties of the MREs are a combination of the matrix properties and the properties of the filler particles. As in any other polymer-based composite, the adhesion and wetting of the surface of the filler particles by the matrix polymer influence the behavior of the composite. With increasing content of magnetizable filler particles, the mechanical behavior of the MRE composite will change remarkably. Therefore, it is important to know the basic composite properties before the influence of the external magnetic field on these properties can be measured accurately. For this study, silicone elastomer filled with carbonyl iron was selected as the studied system on the basis of the good results obtained from the previous tests with different elastomers. The results obtained with this system can also be compared to the results measured by others using different methods for similar kinds of MRE composites [4, 10, 12, 30, 45].

In this study, isotropic and aligned MREs were subjected to bending and compressive dynamic loading and their elastic characteristics as well as their vibration damping properties were studied. The MRE properties were measured both passively (without the magnetic field) and with varying external magnetic field strength. According to the recent theories on MRE behavior, at small and moderate field strength values (well below the saturation level of the filler material) the field –dependent (shear) modulus is proportional to the applied magnetic field strength [10, 12]. This MR effect would be desirable in applications where the stiffness and vibration damping properties of materials need to be controlled actively.

For the maximum MR effect, the filler particles in MREs are usually aligned in strong magnetic field during the curing of the polymer matrix. If no external field is applied during the curing of the composite, the particles have a random arrangement inside the elastomer matrix and the material can be considered as isotropic. The randomness of the particle arrangement depends on the mixing process and the rheology of the mixture before curing. Isotropic materials have typically two independent elastic constants, c_{11} and c_{12}. In the case of isotropic MREs, the values of c_{11}, c_{12} and also of the bulk modulus K are in the same range and of the order of gigapascals. However, the values of the shear and elastic moduli are much smaller, of the order of megapascals. This difference in the magnitude of bulk and shear moduli values is common to elastomers. It means that they can be twisted and elongated with small applied forces but are not compressed that easily. In this study, the MREs were characterized both in bending and compression modes to demonstrate the MR effect with different levels of loading. The longitudinal modulus was studied using ultrasonic technique.

The results of this study show that the aligned MREs have elastic properties quite different from those of isotropic MREs with filler fractions exceeding 15 vol.%. By aligning in magnetic field, the magnetic filler particles are arranged in chain-like structures and they are locked in place during the curing. They also form dipoles, which are magnetically aligned so that the overall energy is minimized. The particles can move quite freely along the magnetic field lines when the viscosity of the elastomer is low in the early stages of curing. As the particles tend to align along the field lines, the particles initially located between the forming chains will be attracted to move to the nearest chain and the area between the chains will become relatively free of particles, as shown in Fig. 11. Consequently, in the cured composite the particle density between the chains is lower than inside the chains. As a result of this particle arrangement, the elastomer matrix inside the chain can be partly trapped between the particles. In contrast to the close-packed particle arrangement inside the chain, the area between the chains consists of matrix elastomer with lower particle density, and the structure of this area is comparable to isotropic MREs (Fig. 10). The particle chains consist of elastomer where the particle density exceeds the density corresponding to the apparent filler volume fraction of the composite. Structurally the composite can, in a way, be compared to fiber-reinforced materials [9].

This structural difference between aligned and isotropic MREs was previously noted by Bellan and Bossis [9]. They studied aligned and isotropic MREs with the same filler content without external field and found that the Young's modulus measured in dynamic tensile testing was much higher for the aligned MREs in the chain direction than for the isotropic MREs. The material between the particles inside the chains can resist deformation more than the same material in isotropic MREs also without the help of applied magnetic field. In this study similar results were obtained. When testing with DMA, the Young's modulus measured in bending for the aligned MREs is higher when the bending axis is in the particle chain direction as compared to the situation where the bending axis is perpendicular to the chain axis (Fig. 43). Also the values of the spring and damping constants and the damping ratio measured for aligned MREs are markedly different in the direction of chains and perpendicular to them (Figs. 21, 23 and 26). The values obtained for aligned MREs differ also from those measured for isotropic MREs with the same filler content (Figs. 20, 22 and 25).

In linearly elastic materials, the elastic behavior of the material reflects the atomic bond forces. The bulk modulus is directly related to the external force required to compress or extend interatomic distances and arises from the internal forces, which seek to establish an equilibrium interatomic distance. A shear stress similarly represents a distortion or bending of atomic bonds. The Young's modulus results from a combination of bond bending and extension/compression. In the case of elastomers, the elastic response is not primarily dependent on the atomic bonds but rather on the coiled backbone structure of the elastomer. During the application of an external load, the molecular coils are "unwound" to the extent that depends on the applied force [43].

When the elastomer is filled with metallic powder, the movement of the molecular coils is restricted to some extent, depending of the filler content. The dynamic stiffness increases as shown in this study. It is known, that as a result of polymer-filler interaction the adsorption of polymer molecular chains on the filler particle surface may reduce the mobility of the polymer segments. On the filler particle surface develops an elastomer shell in which the polymer viscosity and modulus are increased as compared to the basic properties of the elastomer matrix. The very high modulus of the elastomer in the elastomer shell close to the surface of the filler particle decreases gradually with increasing distance from the filler surface and finally it reaches the modulus level of the elastomer

matrix. When two or more filler particles are close enough, they will form agglomerate via a joint elastomer shell in which the modulus of the polymer is higher than that of the polymer matrix. The filler particles can also touch each other. For the filler particle network constructed by the direct contact mode it is believed that the higher energy dissipation of the filled elastomer originates from the breakdown and reformation of the filler particle network [44]. These two mechanisms can be the reason for the increased stiffness and higher energy dissipation of the chain-like structure in MREs. The increased stiffness (Figs. 26, 33, 35 and 38) and energy dissipation (Figs. 21, 23 and 34) of the particle chains is manifested both in bending and compression. The increase in longitudinal modulus is revealed also by studying the velocity of ultrasound in the material (Fig. 40).

In the rubbery stage, the internal friction between the filler aggregates can be the dominant mechanism for dynamic hysteresis in the MREs. When the filled elastomer undergoes dynamic strain, the elastomer in the joint shell may also modify the temperature dependence of the properties of filled elastomers. At a temperature where the polymer matrix is in the rubbery state, but the polymer in the elastomer shell is in the transition state due to either the adsorption of the polymer molecules on the filler surface or to the interaction between polymer chains and filler, the joint elastomer shell will absorb more energy resulting in higher hysteresis [44].

At lower temperatures, the elastomer shell can fall into the glassy state when the elastomer matrix is still in the rubbery or in the transition state. Due to this, the effective filler volume fraction will substantially increase as also the elastomer shell, which is in the glassy state, is hindering the deformation. The elastomer can also be trapped inside the filler particle agglomerates, which act as "cages" and behave as hard filler. This will also increase the effective filler volume fraction in the MRE. For a given polymer-filler system both mechanisms, the direct contact mode and the joint elastomer shell between the filler particles may play part in the formation of the filler particle network [44]. Both of these mechanisms are further enhanced by the application of external magnetic field.

The measurements carried out on aligned MREs with DMA at elevated temperatures show a decrease in zero-field dynamic stiffness and a corresponding peak in damping in a definite temperature range (40 to 60°C). At

room temperature the elastomer shell surrounding the filler particles may be in the glassy state and it may reach the transition state at slightly elevated temperatures. With applied magnetic field, the decrease in stiffness at this temperature is still visible even if the average stiffness is on a much higher level than without the magnetic field. After the slight decrease in this temperature range the stiffness remains on a constant level with increasing temperature when measured in magnetic field with constant strength.

The particle arrangement has a remarkable influence on the composite properties both without and with the applied magnetic field. When modeling the MREs, the elastomer matrix should not be considered as homogenous due to the third phase or elastomer shell surrounding the particles. At higher filler fractions, the particle chains consist mainly of this elastomer shell and trapped elastomer between the particles. The elastomer shell has properties different from the rest of the matrix. The effects of this network structure are more evident at higher filler fractions. The breaking and reformation of the aligned network structure in dynamic loading is sensitive to the strain amplitude but the network can be reinforced by the application of the magnetic field. The MREs are unique composites as the extent of particle networking can be controlled by the direction of the magnetic field and by the magnetic field strength during the curing of the material.

14.2 Dynamic stiffness and moduli of the studied MREs

In this study the basic composite properties of the isotropic and aligned MREs were studied and compared to the properties measured with the applied magnetic field. The dynamic stiffness k was measured for both isotropic and aligned MREs. The aligned MREs were measured in the direction of chains (Direction 1) and perpendicular to them (Directions 2 and 3, see Fig. 15). The stiffness was measured first in dynamic bending, where the loading direction was either parallel to the chains (Direction 1) or perpendicular to them (Directions 2 and 3) and the magnetic field direction was always perpendicular to the direction of the dynamic load. Bending measurements were carried out for isotropic and aligned MREs with 0 to 30 vol.% of Fe. In the bending measurements, a moderate magnetic field strength ranging from zero to 0.3 Tesla was used. Static and dynamic stiffness values of isotropic and aligned MREs with 30 vol.% Fe were

also measured in compression. In compression, the magnetic field strength inside the coil system was varied from zero to values close to the magnetic saturation of the MREs (1 Tesla).

14.2.1 Isotropic MREs

It was noted, that the stiffness of isotropic MREs increased steadily with increasing filler content in the whole studied filler volume fraction range up to 30 vol.% when measured without magnetic field. The magnetorheological effect was observed in isotropic MREs only when the filler content exceeded 15 vol.%. With filler contents over 15 vol.%, in homogenous distribution the particle density was high enough for the particles to interact due to the application of the external magnetic field. The chaining of the particles during curing changed the behavior of the MREs remarkably as compared to isotropic MREs. When measured in the direction of the chains, the MR effect was noted also with the filler contents below 15 vol.%. The particle density in the chain direction was high enough for the particle interaction even with smaller filler contents. In the direction perpendicular to the chains, the MR effect was noted only when the filler fraction was over 15 vol.%, similarly as in the isotropic MREs.

The dynamic stiffness of isotropic MREs measured in bending increased almost linearly with increasing filler volume fraction when measured without the magnetic field. At 30 vol.% filler, the measured values of spring constant were increased by factor of two as compared to those of the unfilled silicone. When measured in magnetic field, a change in stiffness was noted only when the filler fraction exceeded 15 vol.% of Fe. The dynamic stiffness in bending was found to be tuneable with magnetic field at filler fractions between 17 and 25 vol.%. The stiffness was increased by 5% when applying the field strength of 0.13 Tesla and 5% more with the field strength of 0.3 Tesla (Fig. 25). The spring constant values measured for isotropic MRE increased also slightly with increasing temperature in the magnetic field with constant strength (Fig. 29). This can be explained by the fact that the increasing temperature rendered extra mobility to the filler particles, which could then change their position along the magnetic field lines to slightly more optimal locations. However, the stiffness increase in isotropic MREs was only moderate as compared to the aligned MREs with the same filler content.

The dynamic stiffness of isotropic MREs was also studied in compression. In compression testing the stiffness of isotropic MRE with 30 vol.% of Fe was found to increase by 10% when applying the magnetic field strength of about 1 Tesla (Fig. 38). Isotropic MRE did not show any strain dependence of stiffness when studied in compression up to 10% strain amplitude (Fig. 35). This result suggests that no particle network is formed in MREs without the influence of applied magnetic field during curing.

Dorfmann and Ogden [31] have showed theoretically, that the influence of a magnetic field makes the shear response of an isotropic MRE stiffer. This can be seen also in our results, when the filler fraction is high enough. Without a magnetic field, the shear modulus of an isotropic MRE with 30 vol.% of iron is about twice the modulus of the unfilled elastomer. With applied magnetic field, the shear modulus further increases when the filler volume fraction is over 15 vol.%. At filler fractions over 15 vol.% the particle density is high enough to facilitate the interaction between the particles in the magnetic field. The relative increase in shear modulus as compared to the zero-field modulus with the same filler volume fraction is about 10% for the magnetic field strength of 0.3 Tesla (Fig. 42).

The experimental results on the shear modulus for isotropic MREs were compared to the models, which have been used for predicting the shear modulus of elastomer-based composite materials with different filler volume fractions. The models by Guth [32] and Christensen [19] (concentrated suspension model) are developed for composites with defined packing geometry. They take into account only the shear modulus G_0 of the unfilled matrix and the volume fraction of rigid filler particles. Equation (3) can be used for calculating the modulus for an open, non-close packed cubical arrangement of spherical particles [8, 32]. If the composite is stretched, the suspended particles perturb the stresses and strains are set up in the matrix. In the concentrated suspension model by Christensen (Equation (5)) the particle packing arrangement is also assumed to be cubical.

While these two models described above have only two variables, in the three-phase model [19] six variables are needed. In addition to the shear modulus of the matrix, the non-dilute version of the three-phase model by Christensen also takes into account the shear modulus of inclusions and the bulk modulus and the

Poisson's ratio values of both the inclusions and matrix. The values obtained from these three models were compared to the experimental data of this study. It was found that the non-dilute model did fit to the experimental data for the isotropic MRE quite well and hence it can be used for predicting the shear modulus for isotropic MREs with different filler volume fractions. This further suggests that it could also be used as a basis for building a model for the elastic properties of these materials under the influence of magnetic field to replace the current models, which are based on the assumption of a cubical particle arrangement. For creating such a model, the influence of the magnetic field could be difficult to predict on the basis of the magnetic interaction between two or more particles as the particles are randomly distributed in the matrix. When considering the fact that with an applied magnetic field the effective filler volume fraction is actually higher than the volume fraction of bare filler (and it will be constantly increasing with the increasing magnetic field strength), the increase in modulus could be predicted. However, for isotropic MREs the increase of stiffness due to applied magnetic field is only moderate compared to aligned MREs.

The maximum MR effect in composite stiffness existed at the magnetic saturation of the filler particles. According to the measurements with the sensitive SQUID magnetometer, the saturation magnetization of the isotropic MREs studied here was changing with the filler content. It started to occur at the applied magnetic field strength of approximately 0.7 to 0.8 Tesla and the particles were fully saturated at 1 Tesla.

14.2.2 Aligned MREs

The dynamic stiffness of aligned MREs was measured both in bending and in compression. The dynamic stiffness of aligned MREs depends strongly on the loading direction in bending. With the loading direction parallel and perpendicular to the chains (when characterized without external field) the stiffness was found to increase with the filler volume fraction in both directions but in the chain direction the composite was much stiffer (Fig. 26). Without magnetic field, the spring constant values measured in Direction 1 are approximately twice the values measured in Direction 2 (see Fig. 15). The maximum values were found between 25 and 30 vol.% (peak value at 27 vol.%)

of filler. This could be noted in the measurements both without and with the magnetic field. When measured with applied magnetic field there is an increase in stiffness in the chain direction for all studied filler fractions. When measured with the load perpendicular to the chains, the increase in stiffness is smaller and noted only for the filler fractions over 20 vol.%. The increase in dynamic stiffness is larger when the magnetic field is applied in the chain direction as compared to the situation where the field is perpendicular to chains.

In compressive testing, the loading direction was always parallel to the chain direction and also to the magnetic field direction. Only aligned MREs with 30 vol.% of Fe were characterized in compression. The increase in both static and dynamic stiffness with magnetic field was noted in the compressive loading of aligned MREs (Figs. 30, 31, 32 and 33). The measured maximum value for the Young's modulus in static compression was increased by the factor of two from the zero-field value and the dynamic stiffness was increased by 60% of the zero-field value at saturation (at the field strength of about 1 Tesla). Moreover, the static stiffness was found to be tuneable with magnetic field up to the magnetic field strength of about 0.8 Tesla. The increase of stiffness in dynamic compression at saturation is in the same range (60%) as measured for the maximum increase of the shear modulus in other studies on similar composites [4, 10, 13]. The dynamic stiffness was also increased with increasing frequency in the studied frequency range (up to 15 Hz, Fig. 33). The dynamic stiffness was found to be tuneable by magnetic field up to the field strength of about 0.8 Tesla (Figs. 33 and 36).

In aligned MREs the zero-field maximum value of Young's modulus measured in Directions 1 and 2 (see Fig. 15) was found at filler volume fractions between 20 and 27 vol.% of Fe (Fig. 43). When the bending load was perpendicular to the chains, the Young's modulus was much higher than with the bending load parallel to the chains. In the perpendicular direction (Directions 2 and 3 in Fig. 15) the bending deformation is concentrated in the particle chain area. In Direction 1, the deformation occurs mainly in the area between the chains and the measured Young's modulus is from 1 to 1.5 MPa lower than in perpendicular Direction 2 without the applied magnetic field. With the applied magnetic field, a small overall increase in E was noted in Direction 2, but not in Direction 1. The maximum increase in E in magnetic field (1 MPa) in Direction 2 was found at filler fractions between 27 and 30 vol.%. As the Young's

modulus measures a combination of bending and extension/compression, its value is higher when the bending axis is along the filler particle chains. This result is supporting the theory suggesting the similarity of aligned MREs with the fiber-reinforced composites.

The strongly directional elastic behavior of the aligned MREs indicates that the particle arrangement is not cubical as suggested previously [4]. The columnar particle structure is more likely transversely isotropic and belongs to the class of orthotropic materials which have the same properties in one plane (e.g. the *x-y* plane) and different properties in the direction normal to this plane (e.g. the *z*-axis). Such materials are characterized by five independent elastic constants, instead of nine needed for fully orthotropic materials [19]. In aligned MREs, the particle chains are oriented in common distinct direction, but translational order is absent in the plane perpendicular to the columns implying that the magnetic and elastic properties differ in these directions [11].

The composite properties inside the particle chains differ markedly from those in the areas between the chains and also from the properties of isotropic MREs. In modeling these materials, the aligned particle structure should be thought as transversely isotropic rather than cubic. It should be also noted that the elastic properties of the matrix are not homogeneously isotropic as thought previously. The elastomer shell around the filler particles should be considered as a third phase having different elastic properties and even different T_g from the matrix elastomer. The major part of the third phase is located inside the particle chains. Therefore, the highly packed areas in the particle chains could be modeled as fibers having properties different from the matrix. Due to the trapped elastomer between the particles and the third phase, the effective filler content in aligned MREs is considerably higher in the chain direction than in the direction perpendicular to the chains.

The strain dependence of the dynamic stiffness of the MREs is evident for aligned MREs in compression. While the stiffness of the unfilled silicone or isotropic MRE does not change significantly with increasing strain amplitude in compression, a decrease with increasing strain amplitude is noted for aligned MREs as shown in Fig. 35. The non-linear decrease in stiffness is generally known as the "Payne effect" and it is related to the restructuring of the filler particle network. The Payne effect is exponentially increasing with increasing

filler volume fraction [34]. The lack of the Payne effect in isotropic MRE even at a rather high filler volume fraction of 30% suggests that the filler particles are not forming network structures without the applied external magnetic field during the curing. In compression testing, depending on the used coil device a certain amount of strain could be beneficial for the MR effect. When measured with Coil 2, the increase in stiffness with the 2.5% strain amplitude was less than 20% at saturation. With 5% strain amplitude the measured increase in stiffness was 60% at saturation for the same sample. The prestress reduces the distance between the particles in the chain thus reinforcing the network effect.

The particle network can be reinforced by applied magnetic field even at higher strain amplitudes (Fig. 35). The particle network effect has been known for a long time (Payne effect) but the concept could be used also for creating new multicomponent materials with a magnetically aligned and controllable structure. For example, by dispersing the magnetic particles in one elastomer/polymer and introducing this material to another elastomer/polymer in viscous state under applied magnetic field one might be able to create complex, magnetically controllable network structures resembling living organisms.

In this study, filler particles with a rather narrow particle size distribution were used. For further reinforcement of the network effect, fillers with different particle size distributions could be beneficial. The influence of nanoscale particles on the magnetorheological properties combined to micron-sized particles would be an interesting concept for further studies.

14.3 Vibration damping properties of the studied MREs

In literature, the vibration damping properties of the MREs with applied magnetic field have recently been discussed [7, 9, 10, 13, 14, 26, 28, 40, 41, 46]. There are some contradictory results concerning the influence of an external magnetic field on the vibration damping of the MREs. Furthermore, in different studies the damping is found either to decrease or increase with increasing magnetic field strength. No complete explanation for these contradictory results has been introduced as yet.

Several parameters can be used for describing the vibration damping in materials or structures. The often-used factor tan δ (also called as the loss factor η) is defined as the relation between the storage modulus and loss modulus and it describes the extent of energy dissipation in the material. In viscoelastic materials, the viscous damping constant b describes the rate of damping opposing the vibratory motion but its value depends on the dimensions of the vibrating system. The viscous damping ratio ξ gives the ratio of the actual damping to the critical damping of the material. On the basis of previous studies, it is evident that in aligned MREs the storage modulus (shear or elastic) increases with applied magnetic field strength until the filler particles are magnetically saturated [3, 5, 9, 10, 26, 28, 40, 41]. However, only a few studies exist on the influence of the magnetic field on the loss modulus in MREs.

Bellan and Bossis [9] and Shiga *et al.* [26] have stated that both the storage and loss moduli values of MREs increase in magnetic field but that the influence on the loss modulus is smaller than on the storage modulus. In this study, the spring constant as well as the loss factor and damping ratio values were measured and compared at different testing frequencies and with varying strength of the magnetic field. In compression testing of the aligned MREs with 30 vol.% of Fe (when measured with the magnetic field) the elastomer became stiffer (storage modulus increased) but the measured loss factor decreased with increasing frequency. This indicates that the loss modulus is influenced less by the magnetic field than the storage modulus.

The fillers added to polymer systems are known to cause a considerable change in dynamic properties. The change is noted not only in the complex modulus but also in the loss factor. The effects of filler volume fraction in different temperature regions are caused by different mechanisms as the state and behavior of the polymer matrix change with temperature. In this study, the system consisting of silicone elastomer matrix filled with carbonyl iron was studied only in the rubbery regime, where the elastomer elasticity is high and the resistance to strain is low. In rubbery state, the elastomer typically has a low modulus and low energy dissipation. The Brownian motion is so rapid and the viscosity is so low that the molecular adjustment is able to follow the dynamic strain [44]. In the temperature range from 20 to 130°C the damping of isotropic MREs with 30 vol.% of Fe was only slightly influenced by the increasing temperature when measured passively but the damping was increased with

temperature when measured in magnetic field. However, the damping behavior of aligned MREs with the same filler volume fraction was quite different. A peak was noted at temperatures from 40 to 60°C after which the damping decreased when measured passively. When measured with applied magnetic field the damping increased continuously with increasing temperature (Figs. 27 and 28).

In this study it was noted that the loss factor and damping ratio values measured for the aligned MREs without applied magnetic field were notably higher when the dynamic deformation was directed along the particle chains as compared with the loss factor or damping ratio values measured for isotropic MREs with the same filler volume fraction or for the same aligned MREs measured in other directions. In a rubbery regime, the increasing filler volume fraction is shown to increase the loss factor values measured in dynamic deformation [44]. In the MREs the effective filler volume fraction within the particle chains is much higher than the actual filler volume fraction of the composite. The effective immobilization of the elastomer inside the particle chains will make this elastomer to act as a part of the filler material instead of the elastomer matrix. Moreover, the volume fraction of the third phase (harder elastomer shell around the filler particles) is highest in the particle chain. Therefore, the damping is anisotropic in aligned MREs and the measured values are higher in the chain direction.

The damping properties can be studied by using either forced or free vibrations of the vibrating system. The damping has only a minor influence on the response of the system in the frequency regions either well below or well above the resonance, but it is of great importance at frequencies close to the resonance condition. In the case of forced vibrations, the most important damping occurs at or near resonance frequency [20]. In this study, both isotropic and aligned MREs were characterized in the resonance frequency regime in bending mode both without and with magnetic field and the resulting data was fitted to the equation of motion for damped vibrations. The viscous damping constant b and the viscous damping ratio ξ were calculated for aligned and isotropic MREs with different filler volume fractions (Figs. 20, 21, 22 and 23). The damping was also studied in dynamic compression where the loss factor was calculated using the area inside the hysteresis loop (Figs. 32, 34, 37 and 39).

On the basis of the results obtained using different techniques, the damping of the MREs is either increasing or slightly decreasing with increasing magnetic field, depending on the mutual directions of dynamic loading and magnetic field, on the magnitude of strain and on the particle arrangement. In resonance testing, the influence of damping can be seen in the shape and in the peak height of the resonance curve (Figs. 18 and 19). When the MREs were measured in magnetic field, the vibration amplitudes were radically decreased and the resonance peaks were broader than those obtained in zero-field measurements. In compression testing, the surface area of the hysteresis loops was increasing with increasing magnetic field strength (Fig. 32).

14.3.1 Vibration damping of isotropic MREs

In isotropic MREs, the increasing filler volume fraction had hardly any influence on the damping behavior of the MRE when characterized in dynamic bending without the external magnetic field. This indicates that with increasing filler content the composite does not spontaneously dissipate energy by itself but an interactive particle network structure is needed. The measured value of viscous damping constant b did not change with increasing filler volume fraction; it remained on the same level as that of unfilled silicone as shown in Fig. 20. The viscous damping ratio was also staying quite constant with increasing filler volume fraction (Fig. 21). When measured with the magnetic field both the damping constant and damping ratio started to increase with increasing filler volume fraction when the filler volume fraction exceeded 15%. This suggests that the increasing particle density enabled the interaction of the particles in the external magnetic field. The damping ratio increased considerably from the initial value of about 0.16 to the maximum value of 0.26 at the filler volume fraction of 27%. For other filler volume fractions, the increase of the damping ratio was smaller.

In compression testing, the loss factors measured for isotropic MREs with 30 vol.% of Fe increased with increasing magnetic field strength. When the external magnetic field strength was increased up to about 0.8 Tesla, the value of the loss factor was increased to 0.234 from the zero-field value of 0.20 (Fig. 39). In isotropic MREs, the maximal damping is obtained when the filler volume fraction is optimal for the particle interaction (about 27 vol.%) and it can be further enhanced by applied magnetic field.

14.3.2 Vibration damping of aligned MREs

The damping constants and the damping ratios of aligned MREs measured in dynamic bending without the magnetic field were remarkably different when measured in directions parallel and perpendicular to the chains (Figs. 22 and 23). In Direction 1 (see Fig. 15) without the magnetic field, the damping constant increased slightly whereas the damping ratio stayed quite constant with increasing filler volume fraction similarly as in isotropic MREs. When measured with the applied magnetic field, the values of the damping constant and the damping ratio increased first radically with increasing filler volume fraction at volume fractions larger than 15 vol.% and then saturated at a definite level. In Direction 2 both the zero-field damping constant and the damping ratio increased continuously with increasing filler volume fraction up to the maximum value at about 20 vol.% of filler. With applied magnetic field, an increase in damping was found in both directions but it was more pronounced in Direction 1.

Similarly to the isotropic MREs, in aligned MREs measured in Direction 1 an increase in damping with increasing filler volume fraction was found only at filler volume fractions exceeding 15%. In Direction 2 the damping was slightly increased due to the application of magnetic field with all studied filler volume fractions. The greatest increase in damping was observed in Direction 1 (see Fig. 15) between 20 and 30 vol.% of Fe. The damping ratio measured at the resonance frequency increased from the zero-field value of 0.12 to about 0.20 with the applied magnetic field strength of 0.13 Tesla (Fig. 23).

According to the results of the current study the relative change of damping in aligned MREs is remarkably higher when the dynamic load in bending is applied in the chain direction and the magnetic field direction is perpendicular to the chains. It seems that the extent of damping depends strongly on the mutual directions of particle chains, external magnetic field and applied load.

In compression testing, the loss factor values were calculated from the areas inside the hysteresis loops. In our study a small decrease was noted in the loss factor at saturation when the aligned MRE was studied so that the compressive load and magnetic field were applied in the chain direction. With increasing magnetic field strength the loss factor values of aligned MREs first increased when measured with small and moderate magnetic field strength values, but the

actual increase depended on the compressive strain and testing frequency and the results cannot be easily explained. It seems that the damping of the MREs is increased in magnetic field with small and moderate field strength values but decreases near the saturation when the magnetic field and the dynamic load directions are parallel to the aligned structure.

The mechanism causing the material damping in magnetic field is related to the particle density, particle interaction and particle chain orientation in the MRE but it also depends on the elastomer matrix. In isotropic MREs, no change in damping was observed due to the application of a magnetic field if the filler volume fraction was below 15% of Fe. The particle density was not sufficient to facilitate the interaction between the particles. This was also noted for aligned MREs when the applied bending load was parallel to the chains (Direction 1 in Fig. 15) and the deformation was mainly located between the chains. For isotropic MREs with higher filler volume fractions, the damping increased with the increasing magnetic field strength. In aligned MREs, the damping properties in the direction of the chains were different from those measured in the directions perpendicular to the chains both without and with the magnetic field. This can also be the reason for the contradictory results of MRE damping found in the literature.

In aligned MREs the particles are forming chain-like structures along the applied magnetic field lines during the curing of the composite. The dipole particles gathered in the chains attract more dipoles from the nearby matrix, and as a result the areas between the chains can have much lower particle density. Inside the chains, the attractive forces between the dipoles keep the particles close to each other. As the viscosity grows, the formed network of the particles is locked in place. Some of the elastomer is trapped between the particles and cannot deform when external load is applied on the composite. Each particle is also surrounded by the third phase (elastomer shell) as described previously in the context of the stiffness of the MREs. The areas between the chains have no such network structure and they behave similar to the isotropic MREs with lower particle density under external load.

When the aligned MREs are loaded dynamically with applied magnetic field, the field and the loading directions influence the damping properties. If the magnetic field direction is parallel to the chains, the interaction of the particle network is

enhanced. In the chain direction, the material is much stiffer than an isotropic MRE with the same filler volume fraction. If the loading direction in dynamic bending is perpendicular to the chains, the damping is remarkable due to the constant restructuring of the particle network (bending chains). This is somewhat enhanced by the magnetic field: the particles try to retain their original arrangement when the external force is bending the chains (Figs 21 and 23). In this case, energy is dissipated by the constant restructuring of the particle network. Due to the higher characteristic damping of the material, the difference between the zero-field damping and the damping in magnetic field is quite small. When the loading direction in dynamic bending is parallel to the chains, the zero-field damping is small and comparable to isotropic MREs. When the magnetic field is applied, the damping is remarkably increased by the interaction of the adjacent chains. This increase is noted only at the filler volume fractions over 15%, when the particle density is sufficient for efficient particle interaction.

The distance between the particle chains increases and decreases due to the sinusoidal bending deformation when measured in Direction 1 (see Fig. 15). The particle dipoles have now magnetic moment and try to reorientate themselves in the field direction, which is not possible because they are locked in place by the matrix. At the same time the chains are bending and the distance between the different chains is varying, so that the situation for each particle is changing all the time. In this case (our Direction 1) there is a remarkable loss of energy and the damping ratio is changing from the initial value of about 0.12 to 0.20 with the applied magnetic field strength of 0.13 Tesla. The increase in damping rate is also high.

In this case, the damping is tuneable by adjusting the magnetic field strength as shown also by Ginder *et al.* [35, 36]. The results from the compressive testing also support this theory. In compressive testing with Coil 1, the loss factor values increased with increasing magnetic field (Fig. 34). This occurred also in Coil 2 but the increase was much smaller (Fig. 37). In Coil 2, the magnetic field acting on the MRE may not be as uniform as in Coil 1, which could cause different results. The measured loss factor values for aligned MREs with 5% strain amplitude actually decreased at higher magnetic field strength values. This is due to the more effective locking of the aligned particle structure at higher magnetic field strength values.

In addition to the direction of the aligned particle structure, the damping seems to be influenced by the matrix elastomer. This can be seen in the frequency scans at higher temperatures. With increasing temperature in the rubbery regime, the polymer chains have higher mobility and the MR effect in isotropic MREs is increased from the RT level. In aligned MREs this is evident only when the magnetic field is applied in the particle chain direction. Furthermore, the damping properties change in the temperature range of 40 to 60°C, which suggests that the mobility of the particle chains is increasing. The eventual T_g of the shell structure can be located on this temperature range. By exceeding the glass transition temperature, the stiffness and damping properties of the third phase are changing. In the recent models describing the MR effect of the MREs, it is often assumed that the elastomer matrix is isotropic and the matrix deformation is similar in all directions. This is the case in isotropic MREs but in aligned MREs the local fiber-like structures consisting of elastomer with high effective particle density are dominating the behavior.

By optimizing the particle density and by using the areas between the chains for deformation high relative changes in damping can be achieved with moderate values of magnetic field strength. If the deformation occurs mostly inside the chains, the damping is initially very high and it cannot be changed much with the magnetic field. However, in this case the increase in stiffness and storage modulus values can be very high due to the application of the magnetic field. Both cases have potential applications.

15. Conclusions

The damping properties and dynamic stiffness of magnetorheological elastomers (MREs) can be changed by applying external magnetic field in both isotropic and aligned MREs. The dynamic stiffness of isotropic MREs measured passively (without the magnetic field) increases linearly with the volume fraction of the filler. In isotropic MREs both the stiffness and damping increase due to the application of the magnetic field if the filler volume fraction exceeds 15%. In isotropic MREs the stiffness and damping are tuneable with the magnetic field strength when the filler volume fraction is between 27 and 30 vol.%.

In aligned MREs the damping and stiffness depend on the mutual directions between the applied load, magnetic field and the particle chains in the composite. This observation may explain the contradictory results presented in the literature on the influence of magnetic field on the damping properties of MREs. If the dynamic load in bending or compression is applied so that the deformation occurs along the chains, the damping is initially high and the magnetic field has only a small influence on damping. If the load is applied so that the deformation occurs mostly between the chains, the damping is initially comparable to that of isotropic MRE and can be increased significantly by the application of the magnetic field. In the chain direction, the dynamic stiffness of aligned MREs is tuneable in magnetic field up to magnetic field strength values of 1 Tesla. The maximal stiffness increase of 60% in dynamic loading and 100% in static loading can be obtained when the applied magnetic field and the compressive load are applied in the chain direction.

The particle network structure present in aligned MREs has a significant influence on the elastic and damping properties of the composite. The earlier assumptions on the cubical arrangement of particles in aligned MREs seem not to be valid in the light of current results. Inside the chains the effective filler content is much higher than the actual filler content. This is due to the elastomer trapped between the particles and to the third phase (elastomer shell) in the immediate surroundings of the filler particle. By optimizing the particle density and alignment, either the stiffness or the damping of the MRE can be increased by the application of magnetic field.

16. Proposal for future work

The MREs are potential materials for simple active devices, which can be used for controlling and adjusting the stiffness of constructions and structures rapidly and reversibly. However, even these attractive materials will remain in the laboratory until their material properties are fully explored. For accurate simulations and FEM analysis of the structures with MRE components the exact material properties are needed. The elastic constants of aligned MREs should be analyzed with and without magnetic field. For the definition of these elastic constants, ultrasonic techniques combined with traditional mechanical testing can offer a feasible way as shown in this work.

In compressive dynamic loading, the mechanical behavior of the MREs is influenced by several factors. These include the applied preload, loading force and frequency, strain, magnetic field strength, the uniformity of the magnetic field and the mutual directions between the load, magnetic field and the particle chains. In addition to the actual MRE material, these factors should be studied in more detail.

Another important aspect influencing the usability of MREs is the long-time stability of these metal-elastomer composites. The adhesion of the filler particles and the wetting of the particles by the elastomer matrix can be enhanced by applying a suitable particle surface treatment. When using metallic particles in some elastomers like for example natural rubber a dense coating on a particle surface would be beneficial considering the long-term stability of the composite. The coating of the particles will not disturb the magnetic polarization mechanism. It has been recently shown that the silicate-based hybrid (organic-inorganic) sol-gel coatings can protect ferrous materials from oxidation and corrosion. Covalent bonding may be developed between the metallic surface and sol-gel material, which enhances also the compatibility with polymer matrix. Extensive studies focusing on fatigue and creep properties of these composites are still needed before the MREs can be used in actual constructions.

In order to use the MREs as active materials, magnetic field should be brought to the composite. The magnetic field should be uniform and easily controllable. Small or large coil devices like the prototypes used in this study could be used

for controlling the stiffness or damping of the constructions containing active MRE elements. However, due to the free formability of the MR elastomer materials it would be interesting to use them as surfaces, intermediate layers or coatings in some applications. Further studies are needed for designing, creating and controlling such large, magnetically actuated surfaces.

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Title

The elastic and damping properties of magnetorheological elastomers

Abstract

Magnetorheological elastomers (MREs) belong to the group of so-called smart materials, which respond to an external stimulus by changing their viscoelastic properties. Magnetorheological (MR) material can be fluid, gel or solid material. The mechanical properties of the MR materials change when subjected to an external magnetic field. The MREs are interesting candidates especially for the active stiffness and vibration control of structural systems. The aim of this study was to increase the knowledge on the mechanical and viscoelastic properties of isotropic and aligned MREs. The focus was to clarify the changes in the elastic and vibration damping properties of both studied types of MREs when subjected to magnetic field. Isotropic and aligned MREs were prepared from silicone elastomer matrix with varying carbonyl iron content. The MREs were tested in bending and compression modes with sinusoidal dynamic loading. The 3-point bending experiments were carried out using a dynamic mechanical analyzer (DMA) in resonance for both isotropic and aligned MREs where the filler content varied from 0 to 30 vol.%. For characterizing the materials in compression with applied magnetic field, a special coil device was designed. Isotropic and aligned MREs with 30 vol.% of Fe were also characterized in dynamic compression with varying frequencies and strain amplitudes. The spring constant, elastic/shear modulus and damping ratio/loss factor values were calculated on the basis of the measured data with and without applied magnetic field. The results show, that the stiffness and damping properties of both isotropic and aligned MREs can be modified by applying external magnetic field. The damping and stiffness properties of the MREs depend significantly on the mutual directions of load, magnetic field and the particle alignment in the composite.

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Magnetorheological elastomers (MREs) belong to the group of so-called smart materials, which respond to an external stimulus by changing their properties. Magnetorheological (MR) materials include fluids, gels and solid materials. The mechanical and viscoelastic properties of the MR materials change when subjected to an external magnetic field. The MREs are considered as possible candidates for the active stiffness and vibration control of structural systems. The aim of this study was to increase the knowledge on the mechanical and viscoelastic properties of isotropic and aligned MREs. The focus was to clarify the changes in the elastic and vibration damping properties of both studied types of MREs when subjected to magnetic field. The influence of the alignment of the magnetic particles on the composite properties with and without applied magnetic field was also studied.

The stiffness and damping properties of both isotropic and aligned MREs can be changed by applying external magnetic field. The particle network structure of aligned MREs has a significant influence on the elastic and damping properties of the composite. Inside the chains the effective filler content is much higher than the average filler content. This is due to the "trapped" elastomer captured between the particles and to the formation of the "third phase" (elastomer shell) in the immediate vicinity of the filler particle. By optimizing the particle density and alignment, either the stiffness or the damping of MREs can be increased by applying the magnetic field. The performance obtained with the aligned MREs shows potential for commercial applications of tuneable stiffness and vibration controlling elements.