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Development of MREs for strength and fatigue resistance

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1 Introduction

The future of material technology is likely not to lie in the passive conventional materials that have been used to date but in smart materials that adapt to changes in their environments. Elastomeric materials are also becoming “smart”; shape-memory polymers, self-healing polymers, elastomers that change colour in response to stress, are PH-sensitive or temperature responsive, are all examples of new materials that “intelligent”.

A magnetorheological elastomer (MRE), possessing a stiffness that can be tuned to suit specific operating conditions encountered in service could prove useful in many situations. Many interesting ideas have been presented for MREs including seals [1] and valves [2 - 4], base isolation systems for buildings in earthquake zones [5]. Simpler ideas, but perhaps easier to reach fruition, might include using them as dampers or vibration absorbers in laboratories. Sensitive equipment needing protection from vibrations or background noise in their working environment might benefit greatly from the technology.

In spite of a myriad of possibilities, manufacturers have so far been reluctant to utilise MREs in products. This is surprising because their MR fluid analogues are commercially available and have been used in seat suspension systems for trucks [6 - 7] and high-end braking systems [8]. It has been suggested that MRE materials are not strong enough for real world applications and will be useful only in very limited situations. Researchers have reported poor tensile properties [9] and short fatigue lives [10]. It has been reasonably questioned whether the change in stiffness when a magnetic field is applied, the magnetorheological (MR) effect or switching effect, is sufficient to justify the complexity and cost of production. Much of the published literature describes MRE materials of low zero-field modulus (the initial modulus of the material, before a change is induced by the application of a magnetic field) and thus low stiffness, which can exhibit very significant switching effects (up to several hundred per cent). While such materials might be useful in applications where loading is minimal, potential applications, particularly where the MRE is subjected to higher dynamic loading are limited. This text examines some of these issues and how they might be solved.

MREs respond to increases in magnetic flux density, resulting from the application of an external magnetic field, by stiffening. Many of the most significant changes have been in elastomers of low zero-field modulus. If the matrix material is of low stiffness to begin with, the movement of magnetic particles when a magnetic field is applied may deform the matrix and initiate a dimensional change [11 - 13], resulting in a magnetostrictive material.

An MRE consists of an elastomer matrix filled with magnetic particles or powder. On applying a magnetic field to the composite MRE material, magnetic interactions between the particles cause them to pull together and to attempt to align along the magnetic field lines. This leads to an increase in modulus of the material (which is observed as a switching effect when the field is switched on and off). The magnitude of this effect depends on the magnetic flux density of the field so as the flux density increases the modulus also increases and hence a component fabricated from an MRE material becomes stiffer. If the magnetic filler is magnetically soft, as in a material in which the magnetic field can be easily reversed, exhibiting little or no remanence, the increase in modulus is instantaneously reversible. Ferromagnetic powders are most commonly used as fillers in MR materials, with carbonyl iron powder (CIP) being the most widely adopted MRE filler. CIP exhibits a very high magnetic saturation and thus has the potential to contribute a larger switching effect than less magnetic materials [13 - 14].

Research has found that the switching effect can be significantly enhanced if the dispersion of the particles throughout the rubber matrix is anisotropic [16]. While a homogenous dispersion of particles does result in a material that shows a switching effect, Boczkowska *et al.* [16] have found that anisotropic materials exhibit higher switching effects. They described a correlation between switching effect and “anisotropy coefficient”. This anisotropy, in the form of chains of magnetic particles running through the specimen or component, can be achieved by the application of a magnetic field during the curing process which directionalises the particles so that they are oriented along the lines of flux density [9, 17].

Much research has been conducted on MREs with a natural rubber (NR) matrix. The reasons for choosing NR as a starting point when selecting a matrix material were its high tensile and elevated fatigue properties. Even without reinforcement, NR exhibits a high tensile strength compared to most rubber materials, a benefit generally attributed to its ability to strain crystallise. This increase in tensile strength, caused by the high orientation of the crosslinked macro molecules of the network [18], renders vulcanised NR very useful in automotive applications such as engine mounts and suspension bushings.

Unfortunately NR has very poor aging properties and the use of CIP in an NR matrix accentuates this problem because large quantities of iron particles in a natural rubber matrix can accelerate aging [19]. These iron particles tend to have iron oxides on their surfaces. This can lead to increased levels of oxygen being incorporated into the rubber matrix, quickening the rate of oxidative aging [19 – 21]. An attempt to solve this problem by modifying the surface of the CIP particles with silane was made. Two grades of CIP which contained silicon dioxide (SiO₂) on the surface were chosen for silanisation with Si 69. In theory, the silane reaction would form covalent bonds with the OH groups on the surface of the particles and improve dispersion of the particles throughout the rubber matrix, while acting as a coupling device to enhance the bond between particle and rubber matrix. This would require that each particle be completely coated in silica so that a silica shell was formed around individual particles. Unfortunately the silanisation was not successful and on further investigation of the particle surfaces it was discovered that the number of OH sites available for bonding was too few. There was simply not enough organic material on the particle surfaces. While the develop-

ment of a suitable method to modify the CIP particles to compatibilise them with natural rubber would be a significant step in bringing MREs into applications, this would open another sphere of study in the field of chemistry which goes beyond the scope of this work. In consequence, an alternative polymer must be sought.

Synthetic Ethylene-Propylene-Diene (EPDM) is easy to process and is quite resistant to oxidation and aging. EPDM is ideally suited to resist the temperatures experienced by automotive components. At the time of writing, it is also an economical choice, providing favourable properties while being cheaper than many other types of rubber. This makes it a very popular alternative to NR in sealing applications in the automotive and construction industries. However, EPDM has its own limitations: unfilled EPDM gum has a tensile strength of approximately 4 MPa; much lower than that of NR gum (16 MPa). Unlike NR, it does not possess the ability to strain-crystallise when deformed, necessitating reinforcement with substantial amounts of reinforcing fillers such as silica or carbon black, leaving less room for non-reinforcing fillers such as CIP. EPDM shows inferior resistance to crack initiation and propagation and has lower fatigue resistance by comparison with NR [18]. These limitations must be taken into account when developing an EPDM compound.

A material that combined the advantages of temperature and aging resistance offered by EPDM with the tensile and fatigue properties of natural rubber would be very useful to manufacturers and end users. If such a material could be employed as a matrix for MRE composites it would overcome concerns in respect of low zero-field modulus observed in most switchable MREs, the short fatigue lives observed by Zhou *et al.* [22] and the threat of accelerated aging that is usually present in composites filled with iron particles.

2 Preparation of Materials

Background of the research

The NR series of sample compounds, consisted of specimens containing 400 phr (approximately 25 vol.%) of micron-sized carbonyl iron powder (CIP) (BASF Grade SM). Of these compounds, two contained a low concentration of carbon black (5 phr) while the other two had the carbon black content increased to 30 phr to further reinforce the material. Softener was also added to a batch of each of these two recipes so that a significant difference between each of the compounds was their viscosities. These materials were compared to identify the factors that would most readily maximise the magnetorheological (MR) or switching effect.

Thereafter, in order to obtain MRE materials with improved resistance to aging, the focus shifted to EPDM-based MREs. The knowledge gained in the research using the NR materials was employed in designing an initial base compound, EPDM1. Rather than comparing a series of similar recipes with each other, this base recipe, EPDM1 was tested and further refined in two successive iterations in materials EPDM2 and EPDM3. EPDM1 contained a polymer blend of low molecular weight as a matrix filled with 400 phr CIP (22 vol.%). The EPDMs required larger amounts of reinforcing carbon black than the NR MREs for the rea-

sons discussed in Section 1. However, the amount of filler that can be added to a rubber matrix is limited. Large quantities of filler make the mixture powdery and difficult to mix. Temperature can climb very rapidly in the mixer and it must be controlled so that vulcanisation does not begin during mixing. For the first EPDM sample, 15 vol.% carbon black was chosen. EPDM1 had a Mooney viscosity of 38 MU.

A polymer of a higher molecular weight was employed in EPDM2. The amount of CIP in EPDM2 was reduced to 200 phr (15 vol.%) so that the amount of carbon black could be increased to 40 vol.% to improve tensile strength. Unlike carbon black or silica, CIP is a non-reinforcing filler; although it can increase the hardness and viscosity of the rubber compound, it does not contribute to an improvement in the strength of the compound. Due to the high molecular weight of the polymer and the increased amount of carbon black, the viscosity of EPDM2 was increased to 68 MU.

The same high molecular weight polymer was employed in EPDM3 but a lower quantity of a more active carbon black was used. The reduction in the amount of carbon black permitted an increase of the CIP content to 350 phr (18 vol.%), while the higher activity of the carbon black compensated for its lower volume fraction (30 vol.%). As these changes would also increase the viscosity of the mixture, the amount of softener was also increased from 15 vol.% in EPDM1 and EPDM2 to 30 vol.% in EPDM3 in order to aid processing. This kept the viscosity of EPDM3 at a similar level to EPDM2 at 70 MU. The compositions of the materials investigated are given in Table 1.

Table 1: Composition of compounds

Sample	CIP (Vol.%)	CB (Vol.%)	Softener (Vol.%)	Mooney viscosity (MU)	Zero-field shear storage modulus, G'_0 (MPa)
NR1	28	0.5	-	43	3.28
NR2	22	0.5	3.6	28	1.10
NR3	25	2.8	3.5	29	3.41
EPDM1	22	1.3	2.7	38	1.80
EPDM2	15	4.3	3.1	70	1.40
EPDM3	18	2.9	4.7	70	1.72

3 Experimental methodology

The switching effect of magnetorheological materials is often evaluated by observing the increase in the shear storage modulus of a sample material when an external magnetic field is applied. Such tests can be conducted using double lap shear specimens subjected to uniaxial loading or by torsional shear in a rheometer using disc specimens of 20 mm diameter. For the latter, the evaluations were carried out using an Anton Paar Physica MCR 501 plate-plate rheometer, which contained a magnetic cell beneath the lower plate. As the specimens were

subjected to a torsional shear strain of 0.5 %, a magnetic field was switched on and off at intervals and the magnetic flux density increased each time the field was switched on. The response of each of the materials (the increase in shear storage modulus, G') was observed as the magnetic field was applied and strength successively increased. The increase in G' at the highest magnetic flux density obtained, 1 T, was compared with the zero-field modulus of the specimen (in the absence of a field) and recorded as both absolute values and as a percentage of the zero-field modulus. All of the rheometric tests were conducted on anisotropic MREs, specimens that had been vulcanised in the presence of a magnetic field of 0.6 T.

The strength and fatigue properties of each material were characterised by static and dynamic tensile and dynamic uniaxial cyclic testing. Tensile testing was carried out on a Zwick Universal test machine 1445 in accordance with DIN 53504 using S2 (dog-bone) specimens. Fatigue behaviour was investigated by subjecting dumbbell specimens such as those shown diagrammatically in Figure 1 to displacement controlled cyclic uniaxial deformation in an MTS 831.50 high frequency elastomer test system. This allowed the Wöhler (SN) curves shown in Figure 2 to be plotted. The specimens were strained in tension to 60, 80, 120 and 160 % until rupture and the number of cycles to failure recorded. In all cases, these tensile and fatigue tests were conducted on isotropic MRE samples which had been vulcanised in the absence of a magnetic field. This was simply because the apparatus used to vulcanise anisotropic specimens in the presence of a magnetic field was not large enough to accommodate the moulds used to fabricate dumbbell specimens. An investigation using dumbbells vulcanised in a magnetic field would be highly informative and is recommended for future research.

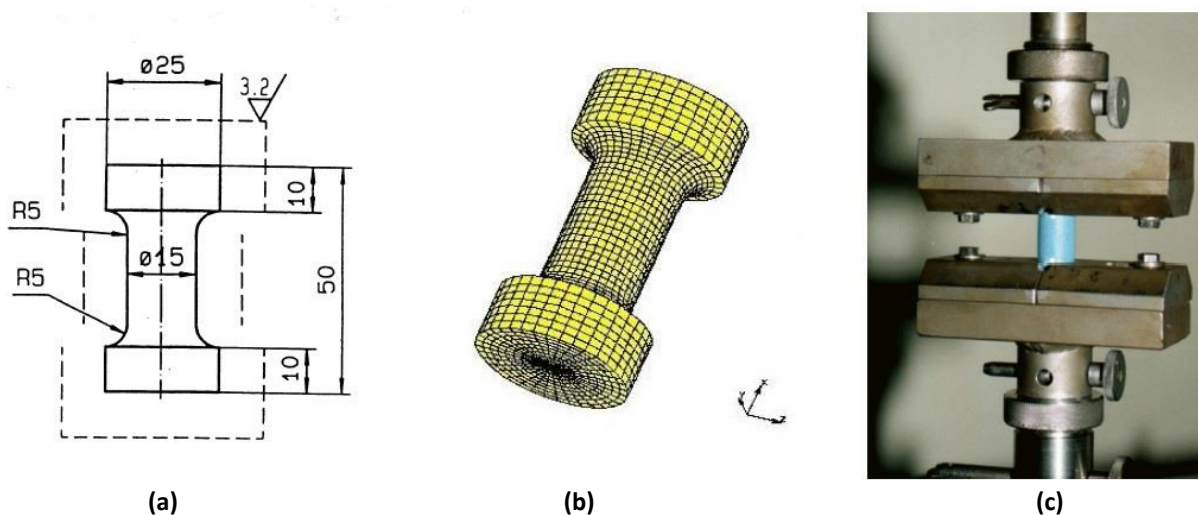


Figure 1: Dimensions of a dumbbell specimen (a), a 3D computer model of the specimen (b) and a specimen in situ during fatigue testing (c)

4 Results and discussion

The effect of the slight variations in the recipes was evident in the zero-field moduli of the NR-based MREs. A clear correlation between switching effect and Mooney viscosity of the materials can be seen in the rheometric results summarized in Table 2. EPDM1, with its lower Mooney viscosity, exhibited a greater increase in the relative switching effect (DG'/G_0) than the more viscous compounds. This confirms the benefit of a low viscosity matrix in assisting particle orientation during vulcanisation. The viscosity of the matrix can hinder the alignment of magnetic particles into chains early in the vulcanisation stage, leading to poorer magnetic particle orientation with them adopting a more homogenous dispersion of the CIP. This results in MRE specimens that tend more to isotropy than anisotropy. While a homogenous dispersion of particles results in a material that shows a switching effect, it has been shown that anisotropic materials exhibit superior switching effects [15 – 17]. Research described in much of the published work used matrix materials of low viscosity containing large quantities of softening oils to reduce rigidity in order to maximise switching effect. Another option to further improve magnetic particle alignment is to add small amounts of retardant to the compound recipes to delay the onset of vulcanisation. Using a retardant in this way increases the incubation time allowing the ideal period for particle alignment to occur [23] while simultaneously slightly reducing the viscosity of the melt. In order to obtain an indication of the tensile strength that might be expected from these materials, tensile testing was conducted on five specimens of the material that exhibited the highest switching effect of the NR2 series. The tensile stress was found to be 14.2 MPa for an elongation at break of 530 %.

The EPDM MREs were subjected to the same rheometric testing as the NR materials. The switching effect of EPDM1 was comparable to that of NR1 and NR3 at approximately 20 %. The tensile strength however, was disappointingly low at 6 MPa. This was deemed insufficient for the applications referred to in the introduction. Rubber materials tend to be chosen because of their ability to be subjected to large deformations without breaking and to recover their original shapes.

All of the EPDM compounds showed similar values for elongation at break but the variations in their recipes led to differences in ultimate tensile strength. The changes led to a doubling of the tensile strength to 12 MPa in EPDM2. At this level, the tensile strength is sufficient for use in the automotive industry. The tensile strength was further improved in EPDM3, reaching almost 16 MPa, which is a significant improvement over what has been reported for MREs in literature to date.

The maximum stresses experienced by the EPDM dumbbells during fatigue testing were plotted against the number of cycles to failure on logarithmic scales to obtain Wöhler curves as shown in Figure 2. Linear trend lines were fitted to the experimental curves. Two extra curves are included for reference: the blue curve is that of an NR material from experimental results. The purple curve is that of an EPDM material from a finite element (FE) simulation.

The remaining three curves are those of EPDM 1 (red), EPDM2 (orange) and EPDM3 (yellow). Generally, they exhibited shorter lifetimes than the other two reference materials. At a maximum stress of 1.28 MPa (log. 0.1 on the y-axis of the graph in Figure 2, indicated by the red line), the EPDM1 dumbbell had a life of merely 100 cycles. EPDM2 had superior fatigue characteristics reaching approximately 3,000 cycles. At a maximum stress of 1.28 MPa the curve for the material EPDM3 surpassed the EPDM reference model reaching 30,000 cycles and approached that of the reference NR material that is currently being used in engine mounts. Indeed one specimen, denoted by a point located to the right of the linear fit, exhibited a life of 63,000 cycles (log 4.8 on the x-axis). The tensile and fatigue properties reported here are significantly higher than anything that has been reported in the literature to date.

However, this increase in tensile strength and fatigue life of EPDM2 and EPDM3 comes at the cost of a reduction in switching effect to only a few per cent. This was attributed to the higher matrix viscosity of the blend containing the high molecular weight polymer and the higher quantities of carbon black required to reinforce the EPDM materials. The Mooney viscosities of these optimised EPDM compounds were almost twice those of the MREs which exhibited the higher switching effects. This returns the focus of the research to the initial question of how to improve the switching effect.

A solution is offered here: by improving the alignment of the magnetic filler particles to enhance the anisotropy of the MREs. Recall the influence of Boczkowska's anisotropy coefficient; the results of the background study proved that the matrix viscosity hinders the formation of particle chains during vulcanisation, leading to a more homogenous dispersion which exhibits a limited switching effect. In these two EPDM recipes, there is ample scope to reduce the viscosity of the material with the addition of softening oil. Retardant can also be added in small quantities to delay the onset of crosslinking. This will maximise the window of time allowed for magnetic particle orientation to occur before mobility is hindered by increasing viscosity as the elastomer cures.

Table 2: Test results of compounds

Sample	G'_0 (MPa)	G'_1 (MPa)	$\Delta G'$ (MPa)	$\Delta G'/G'_0$ (%)	Tensile strength (MPa)	Elongation @ break (%)	Fatigue (cycles)
NR1	3.28	3.88	0.60	18.10	-	-	-
NR2	1.10	1.78	0.68	61.82	14.2	530	-
NR3	3.41	4.06	0.65	19:09	-	-	-
EPDM1	1.80	2.20	0.40	22.00	5.9	560	100
EPDM2	1.40	1.47	0.07	5.00	11.8	525	3,000
EPDM3	1.72	1.78	0.06	3.48	15.6	529	30,000

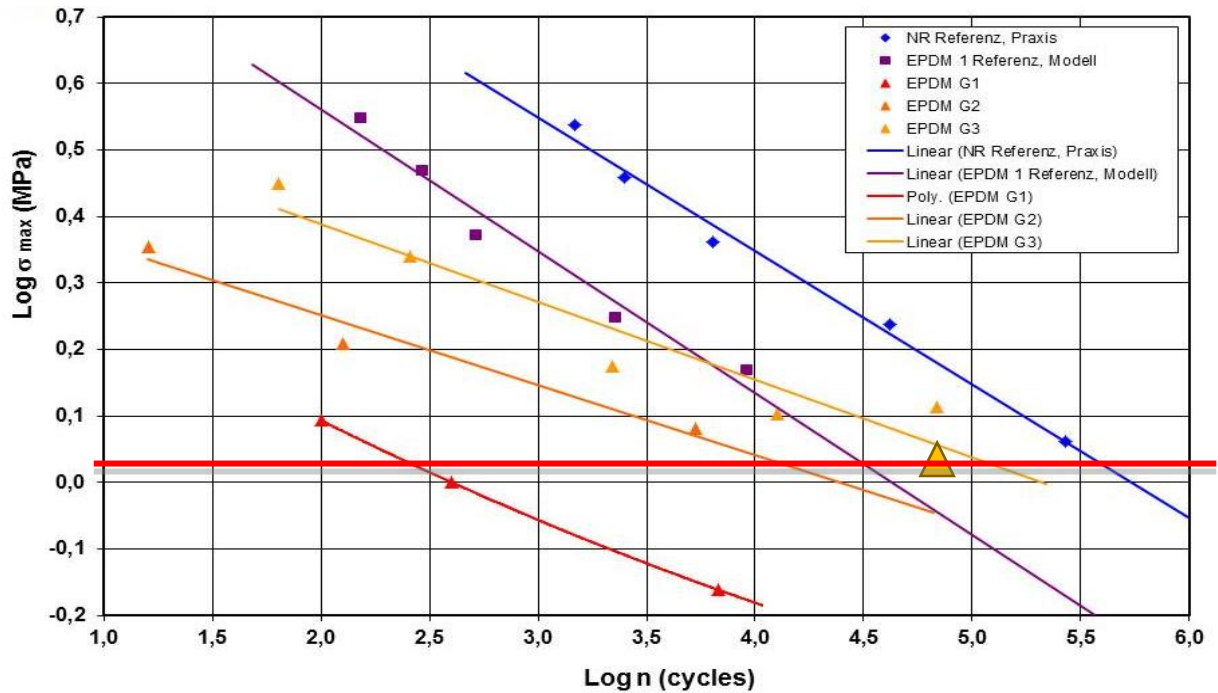


Figure 2: Log. Stress vs. log. cycles to failure for EPDM specimens (linear curve fit)

5 Summary and conclusions

NR-based MREs exhibiting a reasonable switching effect were fabricated and tested. They were strong enough for use in automotive applications but still needed protection against aging. EPDM is a cost-effective material that is frequently used in the automotive industry because of its advantageous range of properties. With these applications in mind, it was a logical progression to the development of EPDM-based MREs. Unlike strain-crystallising NR, EPDM requires reinforcement to render its tensile and fatigue strength suitable for use in most applications. While small amounts of carbon black were sufficient for the NR-based MREs, a trade-off between non-reinforcing CIP and reinforcing carbon black fillers was necessary to imbue the EPDM-based MREs with reasonably good mechanical properties. With a limit on the quantities of fillers that could be added, attention was turned to the matrix material itself and the blend of polymers employed in EPDM2 and EPDM3 were chosen in order to strengthen the EPDM-based MREs by enhancing polymer molecular weight and reinforcement.

However, an unwanted effect of the stronger polymer network was the high viscosity matrix in these compounds which hindered the alignment of magnetic particles early in the vulcanisation process. This led to poorer magnetic particle orientation, resulting in a more homogeneous dispersion of the CIP and consequently produced MRE specimens that were more isotropic than anisotropic. Subsequently the switching effect of these materials was lower than would be obtained in MREs with a low viscosity (say, 40 MU) matrix.

It was not feasible to sacrifice reinforcing carbon black in these compounds, but there are other possibilities open to the rubber compounder. An alternative means of reducing the viscosity of EPDM3 is simply to double the content of softening oil. This would have a slight but minimal negative effect on the tensile properties of the material. The addition of a small amount of retardant to delay vulcanisation and extend the time available for orientation of the magnetic particles into chains would also be beneficial. This would also reduce the modulus of the compound, but the reduction would again be negligible. As in all material design, there is a trade-off to be made in choosing the right combination of properties, but both of these changes would result in the development of an effective magnetorheological compound.

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