Magnetorheological effect for bimodal magnetic elastomers

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INTRODUCTION

Recent years have seen rapid progress in research and development on stimuli-responsive materials, the properties of which change in response to stimuli such as temperature and electromagnetic fields, and application to soft actuators [1] proceeds apace. In Japan in particular, soft actuators that use soft materials to respond to diverse stimuli are under intensive development [2, 3]. This review surveys magnetic soft materials whose properties vary in response to a magnetic field. Such materials change in hardness in response to a uniform magnetic field free from spatial perturbation [4, 5], and exhibit motion such as contraction and expansion or rotation under a non-uniform magnetic field gradient [6, 7]. Characteristically, the magnetic field induces a large force and the response is rapid; and since the field acts directly on the magnetic moiety, the materials have the considerable merit of being capable of actuation without wiring.

Magnetic soft materials are composites of soft polymer materials such as polymer gels, rubbers and elastomers with magnetic particles, magnetic liquids or other magnetic bodies. In general a marked magnetic response can be identified when magnetic particles with a particle size of several μm or more are used. Since magnetic response is in essence a magnetic interaction between the magnetic particles and external field, the magnetic characteristics of the particles can be exploited. For example, using particles of large remanent magnetisation, it is possible to create an actuator that executes rotational motion under magnetisation [7].

Variable viscoelasticity, whereby hardness changes in response to a uniform magnetic field, is manifested when magnetic particles within a magnetic soft material acquire structure. The basic principle is the same as for a magnetic fluid: the magnetic particles form a chain structure aligned along magnetic lines of force, resulting in high elasticity. A necessary precondition for this is hence that the magnetic particles should readily migrate and organize in the interior of the soft material; the viscoelasticity of the matrix and the affinity between magnetic particles and matrix are thus important parameters.

The authors’ group has developed magnetic soft materials capable of large changes in viscoelasticity even in weak magnetic fields from permanent magnets, etc. [8-11]. Overseas too, magnetic soft materials with outstanding magnetic sensitivity have recently been developed [12-15]. However, there is a limit to the amount of change in elasticity modulus for magnetic soft materials made with one kind of magnetic particle. Aiming for higher performance, we have lately been developing materials that function by a novel mechanism. One of these is a magnetic soft material of bimodal type in which magnetic particles are mixed with non-magnetic particles [16-20]. This review surveys the magnetorheological effect in bimodal magnetic soft materials, especially the mechanism of amplification of change in elasticity modulus due to non-magnetic particles.

MAGNETORHEOLOGICAL EFFECT IN BIMODAL MAGNETIC ELASTOMERS

The bimodal magnetic soft materials reviewed here were synthesised by the prepolymer method in the same way as for monomodal material. The prepolymer,
polypropylene glycol, crosslinker, plasticiser, magnetic particles and non-magnetic particles of zinc oxide were mixed and stirred, poured into an aluminium mould and hardened on a hot stage. Reference should be made to the literature regarding the recipe for mixing the various reagents, the reaction temperature and other conditions [9, 11, 17, 18, 20].

Polymers such as poly(vinyl alcohol) [5] and polysaccharides may be used for magnetic hydrogels of bimodal type. The magnetic gel reviewed here has carrageenan as its matrix; carbonyl iron and non-magnetic particles of aluminium hydroxide were dispersed in an aqueous carrageenan solution of approximate concentration 1%, poured into a mould consisting of silicone and glass sheets, and then gelled. Reference should be made to the literature [8, 10, 16] for the gelation conditions, etc.

Magnetorheological effect at low strain

Figure 1a shows the relation between storage modulus and the volume fraction of non-magnetic particles in the bimodal magnetic elastomer at 1 Hz and 10^-4 strain [17]. The results are for addition of non-magnetic particles to a matrix in which 15 vol% of carbonyl iron had been dispersed; the field strengths were 0 mT and 500 mT. The solid line is the storage modulus $G'$ given by the Einstein equation [21] and expressed by the following equation:

$$G' = G'_0 (1 + 2.5 f^{ZnO})$$  

(1)

where $G'_0$ is the storage modulus of the magnetic elastomer without non-magnetic particles. The modulus at 0 mT obeys the above equation, implying that the non-magnetic particles do not form a particle network in the magnetic elastomer. The modulus at 500 mT, on the other hand, increases markedly with increase in the volume fraction of non-magnetic particles. Since they are not magnetised the non-magnetic particles are unable to move spontaneously to form chains and presumably give rise to a high modulus by bridging short chains of magnetic particles.

Figure 1b shows the relation between the change in storage modulus at 500 mT and the volume fraction of non-magnetic particles for the bimodal magnetic elastomer [17]. Below a non-magnetic particle volume fraction of 0.02 there is no amplification of change in modulus due to non-magnetic particles. Above a volume fraction of 0.02 an increasingly marked change in modulus occurs with increase in volume fraction irrespective of the size of the non-magnetic particles. The concentration of carbonyl iron increases by 2% on addition of the non-magnetic particles. The observed change in modulus associated with this increase is shown by the broken line. The modulus changes by at most 0.6 MPa, so the large change in modulus of the bimodal magnetic elastomer is not due to the increase in carbonyl iron concentration.

Figure 2a shows the critical volume fraction of non-magnetic particles $f^{ZnO}$ in the bimodal magnetic elastomer at different magnetic fields [17]. The critical volume fraction decreased with increasing field strength. The critical volume fraction at 500 mT is 0.02 irrespective of the size of the non-magnetic particles, agreeing with the volume fraction at which the change in modulus rises sharply in Figure 1b. At fields of less than 160 mT the critical volume fraction tends to diminish with increase in particle size, hinting at easier percolation the larger the particles.

Figure 2b is a schematic view of the bimodal magnetic elastomer at the critical volume fraction [17]. The number density $N^{ZnO}$ of non-magnetic particles at the critical volume fraction is given by the equation:

$$N^{ZnO} = f^{ZnO} \left( \frac{4}{3} \pi r^3 \right)$$  

(2)

where $f^{ZnO}$ is the critical volume fraction of non-magnetic particles and $r$ is the radius of the non-magnetic particles. The fact that the number density of non-magnetic particles...
at a diameter of 11 μm is 2 orders lower than at 2.1 μm suggests percolation. The number density of magnetic particles is $1.8 \times 10^{10} \text{ cm}^{-3}$, from which the ratios of non-magnetic particles to magnetic particles may be calculated as 206:55 (2.1 μm), 8:55 (5.9 μm) and 1:55 (11 μm), respectively. In a weak field the number density of non-magnetic particles of diameter 2.1 μm is high, which should hinder motion of the magnetic particles, making it difficult for chains to form. Peng et al. [22] have shown by two-dimensional numerical simulation that migration of magnetic particles slows down when non-magnetic particles are added. Some way of achieving good migration of magnetic particles is needed for systems where the number density of particles increases on addition of non-magnetic particles, etc.

**Figure 3a** shows the strain dependence of loss tangent for the monomodal magnetic elastomer at 1 Hz [20]. The loss tangent at 0 mT is 0.20 at low strain and 0.23 at high strain. At 500 mT the loss tangent is constant (0.15) at low strain, increasing slightly (0.38) at a strain of $10^2$. The loss tangent of the monomodal magnetic elastomer thus shows almost no response to a magnetic field.

The strain dependence of loss tangent for bimodal magnetic elastomers at 1 Hz is shown in **Figure 3b**. The loss tangent at 0 mT is 0.30 at low strain and increases to 0.5 at high strain. At 500 mT it is 0.05 at low strain and rises sharply (>30) at a strain of $10^1$. Thus, the loss tangent of the bimodal magnetic elastomer demonstrates an “amphoteric” sensitivity to magnetic field, decreasing at low strain and increasing at high strain. The strain at which field sensitivity switches from negative to positive shifts to lower strain as the field strength increases.

**Figure 4a** illustrates the mechanism of the amphoteric response of loss tangent in bimodal magnetic elastomers [20]. At low strain without a magnetic field, a particle network is formed from magnetic and non-magnetic particles: the storage modulus, which is $1.1 \times 10^4 \text{ Pa}$ for the monomodal magnetic elastomer, increases about 8-fold simply on addition of 15 wt% of zinc oxide. At high strain the modulus of the bimodal material is the same as for the monomodal material, indicating that the composite particle network breaks down completely under strain (**Figure 4b**). In a magnetic field, the low strain storage modulus is $6.0 \times 10^6 \text{ Pa}$, higher than...
the $8.2 \times 10^4$ Pa modulus in the absence of a field and 
the $7.3 \times 10^5$ Pa modulus of monomodal material in a 
field (Figure 4c). It may hence be supposed that a chain 
structure of non-magnetic and magnetic particles has 
been formed. This chain structure would constrain the 
flow of magnetic and non-magnetic particles, and so 
elower the loss tangent. At high strain, the modulus of the 
bimodal material becomes the same as for monomodal 
material, indicating that the chain structure embedding 
non-magnetic particles collapses completely under strain. 
Chain structure consisting of magnetic particles alone 
remains fully intact.

Figure 5a [16] plots the magnetic field sensitivity of 
storage modulus in a bimodal magnetic gel at 1 Hz 
under a strain of $10^{-4}$. The matrix is a hydrogel of the 
polysaccharide carrageenan, and the non-magnetic 
particles are aluminium hydroxide. A field of 500 mT 
is applied every 60 sec. A large change in modulus is 
observed when the ratio of non-magnetic particles to 
magnetic particles is zero ($r=0$). When $r=1$, on the other 
hand, the gel is unresponsive to the field, as would be 
expected. When $r=0.58$ and 0.82, the modulus after 
the first application of the field is roughly 2 kPa lower 
than before application, suggesting that the particle 
network comprising magnetic and non-magnetic particles 
breaks down in the field. This effect is not seen in the 
second application of the field, showing that the structure 
is unaffected.

Figure 5b plots the relation between the storage 
modulus of the bimodal magnetic gel and the ratio of 
non-magnetic particles to magnetic particles [16]. The 
modulus at 0 mT is independent of the particle ratio, 
suggesting that, as in the previously described case 
of zinc oxide, the aluminium hydroxide is well dispersed 
in the matrix. Surprisingly, the high modulus is maintained 
without substitution of 34 vol% of the carbonyl iron by 
aluminium hydroxide. This suggests that the magnetic 
interaction between carbonyl iron particles extends over a 
range of 4-6 μm (equal to 2-3 non-magnetic particles).

The relative permeability $\mu_r$ of the bimodal magnetic 
gel can be written as follows [16]:

$$\mu_r = \mu_{CI} + \left(1 - \mu_{CI}\right) \mu_{CA}$$

(3)

where $\mu_{CI}$ and $\mu_{CA}$ are the relative permeabilities 
of carbonyl iron and carrageenan, 5.48 and 1.0 
respectively. Moreover, the change in modulus $\Delta G'$ due 
to magnetic interaction in the magnetic gel is given by 
the following equation [18].

$$\Delta G' = \mu_r \mu_0 (\sigma E)^2$$

(4)

where $\mu_r$ is the relative permeability of the magnetic gel, 
$\mu_0$ is the vacuum permeability, $M$ is the magnetisation 
of the magnetic gel, and $f$ is the volume fraction. The 
theoretical value of change in modulus $\Delta G'$ due to 
magnetic interaction may thus be found on substitution of $\mu_r$, 
between $\mu_0$ and $M$, of the nuclear magnetisation curve, 
into Equation (4); clearly, the large value of $\Delta G'$ thus calculated cannot be accounted for by magnetic 
interaction alone. It was also found that the use of 
aluinium hydroxide of lower density than the magnetic 
particles achieves a weight reduction of 21% without 
impairing the magnetic field sensitivity of the modulus.

Magnetorheological effect at high strain

Figure 6a shows the stress-strain curves at 0 mT and 
320 mT for a monomodal magnetic elastomer [18]. The 
stress at a strain of 0.2 doubles on application 
of the magnetic field. A similar result is obtained at 
a compression rate of 100 mm/min, close to the rate 
when an object is actually pressed with the finger. The 
stress-strain curve for the bimodal magnetic elastomer 
is shown in Figure 6b. The stress at 0 mT field at 0.2 
strain is almost the same as for the monomodal magnetic 
elastomer. The stress at 0.2 strain increases six-fold on 
application of the magnetic field. A marked increase in 
stress is also seen at large deformation.

Figure 6c shows the relation between the Young’s 
modulus and volume fraction of zinc oxide in bimodal 
magnetic elastomers [18]. The Young’s modulus at 0 mT 
obeys Equation (1). The Young’s modulus at 320 mT 
increases with the volume fraction of zinc oxide, with a 
sharp increase at a volume fraction of about 0.06, which 
is presumably the percolation threshold for the linking of
incomplete chains of carbonyl iron by zinc oxide. The critical volume fraction in the bimodal magnetic elastomer shown in Figure 2a is 0.07, which shows close agreement notwithstanding the different volume fraction of carbonyl iron. The Young’s modulus changes by a factor of 1.8 in the monomodal case and 5.8 in the bimodal case. The storage modulus in the linear viscoelasticity region changes by a factor of 45 in the monomodal case and 86 in the bimodal case. Thus, although the factor is one order lower, the effect on Young’s modulus can be amplified three-fold just by mixing with around 10% of non-magnetic particles.

Figure 7a shows the magnetic sensitivity of electrical resistivity for bimodal magnetic elastomers, as observed at an applied voltage of 50 V [18]. A field of 320 mT was applied every 60 sec. During the first 60 sec, an increase in resistivity is observed due to electrical polarisation of charged impurities. On application of the magnetic field, the resistivity decreases by 2.36 GΩcm in the monomodal case and 0.78 GΩcm in the bimodal case. The resistivity of zinc oxide is of the order of kΩcm, at the semiconductor level. Thus the interposition of zinc oxide particles between chain structures of magnetic particles is also evident from the response of electrical resistivity (Figure 7b). Assuming unidimensional electrical conduction, the resistivity \( \rho_{\text{obs}} \) of the magnetic elastomer can be written as follows using the resistivity \( \rho_c \) of the chains and resistivity \( \rho_i \) of the insulating layer present between the chains [18]:

\[
\rho_{\text{obs}} = \frac{\xi_i}{\xi_c} \rho_i + \left(1 - \frac{\xi_i}{\xi_c}\right) \rho_c.
\]

where \( \xi_c \) is the characteristic length of the chain and \( \xi_i \) is the characteristic length of the insulating layer. Since the resistivity \( \rho_c \) is negligibly small compared with \( \rho_{\text{obs}} \) and \( \rho_i \), the length \( \xi_i \) may be written \( \xi_i = \frac{\rho_{\text{obs}}}{\rho_i} \xi_c \). The characteristic length \( \xi_c \) of the insulating layer thus calculated is 0.12 \( \xi_c \) in the monomodal case and 0.36 \( \xi_c \) in the bimodal case. Hence, 27% of the magnetic particles in a single chain were replaced with non-magnetic particles [18].

Figure 8 shows photographs of the response when the elastomers are compressed at 30 N (3.1 kgf) [18]. In the absence of a magnetic field, both the monomodal and the bimodal magnetic elastomers are greatly deformed. When a permanent magnet of 320 mT is placed beneath the magnetic elastomers, the monomodal magnetic elastomer is greatly deformed whereas the bimodal
magnetic elastomer containing 9.6 vol% of zinc oxide barely deforms at all.

CONCLUSIONS

The magnetic field sensitivity of bimodal magnetic elastomers has been reviewed here. It was shown that, owing to the formation of a chain structure of magnetic particles linked via non-magnetic particles, field sensitivity improves dramatically simply on adding several vol% of non-magnetic particles. Because of the large effect on elasticity modulus, a change in modulus of the same order as in conventional material is obtained at low field strength. Since they are of lower density than the magnetic particles, the non-magnetic particles used in the bimodal magnetic elastomer can contribute to reduction in weight of the material or device. The materials should be useful as haptic devices of variable texture and as vibration control devices able to damp vibrations across all frequencies. Research aimed at practical application is continually advancing, and high strength bimodal magnetic elastomers have been installed in experimental railway cars [20]. Magnetic field equipment and techniques of composite formation for more efficient modification of elasticity modulus are also being studied with a view to early practical deployment.

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REFERENCES