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Hysteresis of the viscoelastic properties and the normal force in magnetically and mechanically soft magnetoactive elastomers: Effects of filler composition, strain amplitude and magnetic field

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ABSTRACT

Hysteresis in dynamic modulus, loss factor and normal forces of magnetoactive elastomers (MAEs) comprising various proportions of small (3–5 μm) and large (50–60 μm) ferromagnetic particles are experimentally studied using dynamic torsion performed at a fixed oscillation frequency in varying DC magnetic fields. It is shown that hysteresis is a characteristic feature of MAEs observed both under increasing/decreasing magnetic field strength and increasing/decreasing strain amplitude. This hysteresis is attributed to the specific rearrangement of the magnetic filler network under simultaneously applied magnetic field and shear deformation. Rheological properties of the magnetic filler network formed in the magnetic field and, therefore, the rheological properties of MAEs depend strongly on the filler composition and the magnetic field magnitude. Larger magnetic particles and higher magnetic fields provide stronger magnetic networks. Both factors result in the extension of the linear viscoelastic regime to larger strain amplitudes and lead to higher values of shear storage and loss moduli. It is found that the hysteresis width maximises at an intermediate magnetic field where it is attributed to the balance between elastic and magnetic particle interactions. This is apparently where the most significant restructuring of the magnetic network occurs. The hysteresis width decreases with increasing fraction of large particles in the magnetic filler. The loss factor grows significantly when the magnetic network is physically broken by large strains $\gamma > 1\%$. A huge (more than one order of magnitude) increase of normal force at maximum magnetic field strengths is observed. It is predicted that any physical quantity depending on the internal structuring of the magnetic filler should demonstrate hysteresis either with a changing magnetic field and constant deformation amplitude or under variable deformation in a constant magnetic field.

1. Introduction

Mechanical hysteresis of an elastomer (rubber) specimen is a well-known phenomenon in physics and engineering [1]. It is manifested in the stress–strain curve, where a somewhat different dependence is obtained for the loading of a rubber specimen from that recorded on retraction. Mechanical hysteresis is due to energy expended as internal friction during the loading which cannot be recovered on unloading. The hysteresis losses are represented by the area between the loading and the relaxation curves. Most rubbers contain fillers, particulate solids, which are embedded into the elastic matrix. It is well known that such fillers increase hysteresis losses.

Recently, much attention has been paid to the so-called magneto-active elastomers (MAE) comprising μm-sized ferromagnetic particles dispersed in an elastomer matrix. If an external homogeneous magnetic field is applied to the MAE specimen, the particles are magnetized and rearrange

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themselves within the elastomer leading to deformation of the specimen [2–7], i.e. magnetostriction. Whether the specimen shrinks or dilates depends on the composite microstructure, applied mechanical load and sample shape [6,7]. Usually, a specimen is elongated. The physical reason for the deformation is the forces acting on magnetized particles. In this sense the application of a magnetic field has a similar effect to mechanical loading, therefore it can be expected that there would be hysteresis of sample elongation as a function of the magnetic field. Indeed, considerable hysteresis of longitudinal magnetostriction (~16%) with the magnetic field applied has been observed in elastically soft MAE [3]. Similar phenomena have been reported for elastic ferromagnetic composites with a porous matrix [4] and for a ferromagnetic composite with a dense elastomer matrix [5]. Importantly, the iron particles used in Refs. [3–5] were practically free from magnetic hysteresis (negligible loop in the magnetization M versus magnetic field strength H characteristic). Consequently, hysteresis behaviour of longitudinal magnetostriction as a result of the applied magnetic field strength could not be attributed to magnetic moments of the filler particles in the magnetic field. The explanation offered in Ref. [4] is similar to the "Payne" or "Mullins" effect, namely that of slippage of the adsorbed hydrocarbon chains along the filler surface. If a magnetic field was first increased and then retracted back to the initial value, the particles and the chains between them do not immediately resume their original position. The energy which was dissipated by friction between particles during the magnetic field strength increase cannot be recuperated and any return to the original ordering requires further energy. As a result it can be assumed that there is no guarantee of direct correlation between filler particle position and magnetic field strength during increase and decrease of the magnetic field. If the microstructure of filler particles is different, the relevant mechanical characteristics, e.g. the complex shear modulus $\underline{G} = G' + iG''$, where G' is the shear storage modulus and iG'' is the imaginary shear loss modulus, can also be different. In the literature, the magneto-sweep usually shows one curve for $\underline{G}$-components as a function of increasing magnetic flux density B and the possibility of magnetic hysteresis is ignored. We are aware of only one paper [8], where a hysteresis as a function $G(B)$ for one sample of highly compliant MAE is reported.

There is a striking similarity between the structuring of magnetic filler particles at constant strain amplitude γ with the increasing/decreasing B and at the constant B with the increasing/decreasing strain amplitude γ. In both cases the hysteresis of magnetic-field dependent physical quantities can be expected, since the particles do not necessarily resume their original position. Formation and reorganization of magnetic microstructures in magnetic fields have been directly observed in magnetic elastomers and gels by several groups [8–13]. Recently, it has been recognized that this reorganization can take place under shear force in a magnetic field. Simultaneously applied magnetic field and shear strain promote particle rearrangement in order to form tighter aggregates. This effect leads to pronounced cyclical stress hardening [12–14]. Such particle rearrangements, namely string formation and breaking, have been directly observed in magnetic gels comprising small fractions of magnetic particles [12]. At high concentrations, the magnetic particles could form a three dimensional network. Similar processes of particle rearrangement could change the structure and the mechanical strength of this network and thus, influence the magnetic response of MAE.

Strain dependence of magnetorheological (MR) characteristics in highly filled MAE of various compositions and anisotropies and their evolution with cyclically increasing and decreasing strain amplitudes have been studied recently [14], where the impact of matrix elasticity and magnetic interactions on filler alignment have been elucidated. It has been shown that the dynamic modulus saturates after several cycles of shear loading. Furthermore, the pronounced hysteresis behaviour with the loading-unloading strain amplitude has been observed.

For non-magnetic particle filled polymer composites, it has been shown that their mechanical properties are influenced by the particle size, the particle content and the particle-matrix interfacial adhesion [15]. For a given particle loading, smaller particles have larger total surface area and could contribute to more efficient stress transfer mechanisms. In the case of magnetic particles their induced magnetization affects the strength of their interactions. Furthermore, a tighter packing of the filler particles in aggregates could be expected when small and large particles are mixed together. Magnetorheological composites consisting of two entirely different magnetic filler particles (micro- and nano-sized particles) at fixed total concentration have been recently studied [16].

The purpose of this paper is to investigate details of the elastic and magnetic hysteresis of viscoelastic (dynamic modulus and loss factor) properties and the normal force of mechanically soft MAEs comprising magnetically soft particles. In particular how the filler composition affects both the MR effect and the hysteresis are investigated. The importance of the latter issue is undoubtedly of significance, both for the fundamental understanding of particle rearrangement processes and for potential applications.

The paper is organized as follows: In the experimental section sample preparation and details of the rheological study are described. In the following section, results regarding the rheological properties and normal force of MAEs in increasing-decreasing magnetic fields and under cyclic increasing-decreasing strain amplitudes are presented and discussed. The conclusions are drawn in the final section.

2. Experimental

2.1. Materials and sample preparation

The polymer matrices have been fabricated using the silicone compound SIEL produced by the Russian State Institute of Chemistry and Technology of Organoelement Compounds (GNIIChTEOS). The compound SIEL is commercially available and its composition has been described in detail elsewhere [3,9,17,18].

Carbonyl iron particles of two different average sizes (3–5 μm and 50–60 μm diameter) have been used as the magnetic filler. Mass percentage of the filler has been maintained constant (83.5 ± 0.5 mass% corresponding to the volume filler concentration of 39.3 ± 0.7%) for all fabricated samples, whereas the proportion of small and large particles has been varied. The composition of the synthesized samples is summarized in Table 1.

MAE samples were prepared from silicone compound SIEL mechanically mixed with magnetic particles for a duration 5 min at room temperature. The mixture was poured into the Teflon mould and cured at 150 °C for 40 min. A weak external magnetic field of 80 mT was applied during curing to prevent particle sedimentation. Disk-shaped samples of 19.8 mm diameter and of 1.65 ± 0.20 mm in thickness were obtained for the rheological study. Due to particle sedimentation the sample comprising only large particles could not

Table 1
Sample composition.

Sample #	N1-0	N2-25	N3-52	N4-64	N5-82
% of large particles	0	25	52	64	82