Viscoelastic Response of Magnetorheological Suspensions

Andrei Munteanu, M.Sc., Ph.D.

Doctoral Thesis Summary

Tomas Bata University in Zlín

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Centre of Polymer Systems

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Viskoelastická odezva magnetoreologických suspenzí

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DEDICATION

These 4 years and 3 months are dedicated to Νικολέττος Μερκούριος "Nikole'ttos Merkou'rios" a childhood friend who was lost during a car accident during this Ph.D. His music and memories followed me in this journey.

"Χρόνου φείδου μάγκα, κάποτε οι ώρες θα τελειώσουν"
"Spend your time wisely dude, eventually the hours will run out"

ΙΧΩΡ - Εντρυφώ by Nikolletos Merkourios

ABSTRACT

Smart materials are usually referred to the systems that can alter some of their properties when exposed to an external stimulus. Magnetorheological fluids (MRFs) and elastomers (MREs) are categorized as good examples of smart materials as they are able to change properties such as their mechanical properties and conductivity under the influence of a magnetic field. This topic has grown significantly both in the fundamental research and applications however, there is a big gap in between as in fundamental research only one type of flow is studied while in real applications, more types of flow are present. This thesis tries to marry the fundamental research of MRFs and MREs with their applications. Different types of MRFs were developed based on specific applications. To be specific this thesis includes the development of conductive and magnetic composites based on polypyrrole (PPy), magnetite nanoparticles, nickel and iron microparticles (carbonyl iron) which were used as an MRF. The particles are used as electrical devices that are able to control the resistance and capacitance under the influence of an external magnetic field. Additionally, due to the ability of the PPy to be synthesised in different morphology, dimorphic MRFs were investigated filling an important gap of the field. Due to the rise of MRE-based materials, it is important to prepare recyclable MREs. Thermoplastic-based MREs were prepared based on several types of matrices including a thermoplastic polyurethane and a propylene-based elastomer supplemented with ethylene groups. Both types of MREs are able to be reprocessed several times. The mechanical properties after processing were similar to the initial batches. The reprocessing was simulated by studying the time dependency of the MREs and it was found that the matrix can interact and bond with the magnetic particles.

Keywords: *magnetorheology, carbonyl iron, nanotubes, polypyrrole, magnetorheological elastomers, magnetorheological fluids*

ABSTRAKT

Chytré materiály jsou obvykle označovány jako systémy, které mohou změnit některé ze svých vlastností, když jsou vystaveny vnějšímu podnětu. Magnetoreologické kapaliny (MRF) a elastomery (MRE) jsou příklady takových inteligentních materiálů, protože jsou schopny měnit vlastnosti, jako jsou jejich mechanické vlastnosti a vodivost, pod vlivem magnetického pole. Tyto materiály se těší výrazné pozornosti jak v základním výzkumu, tak v aplikacích, stále však existují možnosti jejich dalšího vylepšení. Tato práce se snaží spojit základní výzkum MRF a MRE s jejich aplikacemi. Na základě specifických aplikací byly vyvinuty různé typy MRF. Konkrétně tato práce zahrnuje vývoj vodivých a magnetických kompozitů na bázi polypyrrolu (PPy), nanočástic magnetitu, mikročástice niklu a železa (karbonylové železo), které byly použity jako MRF. Takový systém lze použít pro elektrická zařízení, která jsou schopna řídit odpor a kapacitu pod vlivem vnějšího magnetického pole. Navíc, vzhledem k možnostem syntézy PPy v různých morfologiích, byly zkoumány dimorfní MRF, které vyplňují důležitou mezeru v oboru. S ohledem na nárůst materiálů a aplikací na bázi MRE je důležité připravovat recyklovatelné MRE. V práci byly připraveny MRE na bázi termoplastů na základě několika typů matric včetně termoplastického polyuretanu a elastomeru na bázi propylenu doplněného ethylenovými skupinami. Oba typy MRE lze několikrát přepracovat. Mechanické vlastnosti po zpracování byly podobné jako u původních šarží. Přepracování bylo simulováno studiem časové závislosti MRE a bylo zjištěno, že matrice se při tomto procesu může interagovat a vázat s magnetickými částicemi.

Klicova slova: *magnetoreologie, karbonylové železo, nanotrubice, polypyrol, magnetoreologické elastomery, magnetoreologické tekutiny*

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Contents

1. INTRODUCTION

1.1 Origins

The aim of this introduction part is to provide a reader interested in magnetorheology with a short description of the basic concepts of the science together with some basic physics from related fields. Magnetorheology is a complex word of Greek origin which combines the terms “magneto” i.e. “μαγνήτο” [maghni’to] and “rheology” i.e. “ρεολογία” [reologhi’a] with the latter being composed of two more words “ρέω” [re’o] which means the verb flow and “λόγος” [lo’ghos] which according to the most common translation means “reason” but in this case, it means “speech”, which is typical for definitions of sciences. Thus, rheology is the science that studies flow. “Μαγνήτο” comes from “Μαγνήτης” [Maghni’tis] (Magnet in English) which should be written with capital as it literally means the person who is descended from a specific Ionian tribe called “Μαγνησία” [Maghnisi’a] (Magnesia in English) which was colonized from the Magnesia of Thessaly in Greece. The meaning of the magnet nowadays comes from the Magnets of Ionia whose lands were rich of the mineral magnetite and are currently in Turkey. The term magnetorheology is the science of the flow behaviour of materials with magnetic properties, although the term does not have an official definition. Magnetorheological (MR) is thus a material whose rheological properties can be altered with a presence of a magnetic field. For the second and last word of this thesis’ title “suspension” describes the systems used for the thesis as unfortunately typical magnets are solid and will not flow in our lifetime for temperatures below their Curie temperature. Thus, the systems described here are suspensions of solid magnetic particles suspended in a fluid. However, the more appropriate term describing the systems used in this thesis would be dispersions.

1.2 Introduction to Magnetorheology and Magnetorheological Materials

The MR dispersions used in this thesis can be divided into two categories. On one hand magnetorheological fluids (MRFs) and on the other, magnetorheological elastomers (MREs). The former is a suspension consisted of ferromagnetic particles with size (in terms of hydrodynamic radius) higher of that of a micrometer [1]. These particles are dispersed in a fluid, thus a viscous medium, which depends on the desired applications [2]. A suspension, or more appropriately a colloid, of magnetic particles in the nanometer range is given the term ferrofluid which may undergo different magnetic phenomena such as Neel’s relaxation. The regime between ~100–1000 μm is unexplored due to the large remanent magnetization that the particles of that size have [3].

Magnetorheological elastomers on the other hand are also dispersions of magnetic particles with the same size criteria, however the dispersed phase is an elastomer matrix thus a viscoelastic medium [4, 5].

The MR dispersions are categorized as smart materials. Their most common applications take advantage of the material's ability to tune its mechanical properties upon exposure to a magnetic field. The altering of the mechanical properties happens within a millisecond. Once exposed to a magnetic field, the magnetic particles align in a column-like structure to minimize their free energy (see **section 2.3**). These columns add an additional elastic contribution, transforming the fluid in a soft solid or a yield stress fluid which is usually orders of magnitude higher than the stresses reached at the proportional shear rates when no magnetic field is applied [6]. The fraction of the material's shear stress with/without the presence of a magnetic field is commonly referred as the "MR effect" and it is the most important quantity of an MR material. Depending on the imposed magnetic field, the MR effect varies from the order of unity and can exceed four orders of magnitude [7]. This ability to alter the internal structure of the material is utilized in several applications with most notable including dampers, valves, and robotics [8-10]. Both types of MR dispersions are facing severe challenges which will be discussed later in detail [11].

2. THEORETICAL PART

2.1 Magnetic Particles

The most commonly used magnetic particles for MR-based research are by far the Carbonyl Iron (CI) particles due to their high saturation magnetization (*M*s) of ~200 emu/g which is a key quantity for the MR performance of the suspension. For comparison, magnetite-based particles which are the most commonly used in commercial magnetic suspensions may have ~4 times lower *M*s as depicted in **Fig. 2.1**. Despite having the highest *M*s, magnetite particles saturate faster (for lower fields) which is a useful property that is not utilized in literature. For that reason, both CI and composite magnetic particles based on magnetite are used in this thesis.

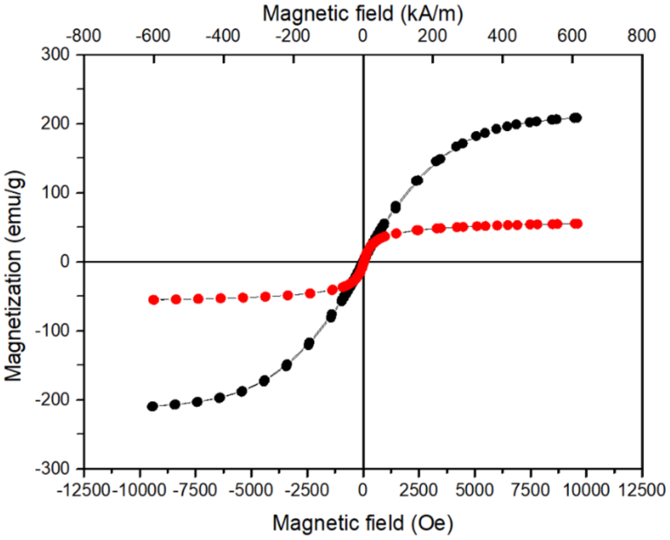

Figure 2.1 Vibrating sample magnetometry for CI CN grade (black) and a magnetite-based composite (red; PPy 6 later in this thesis).

The size of the particle affects its *M*s which is generally reduced with size as displayed in **Fig. 2.2a**. Particles in the range of the nm have a single domain which allows them to obtain the superparamagnetic status either through Neel's or thermal magnetic relaxation, or through thermal rotation. Larger particles in the range of a 100 nm display higher values of *M*s due to surface effects however, the presence of just a handful domains creates a large remanence which creates strong attractions between the particles during off-state. This results in the irreversible agglomeration of the magnetic particles which diminishes the system's stability. Lastly, a further increase of the particles size will result in the shrinkage of the permanent magnetization as the domains become too many and cancel each other out and in the end a net (practically) zero coercivity is achieved. Thus, the particles of this size display an ultra-soft ferromagnetic-like behaviour. The *M*s for particles of this size is further increased and so the MR performance which establish them as great candidates for engineering applications [12]. The size effect in terms of the coercive field is shown in **Fig. 2b** together with the range where a dispersion consisted of such particles would be considered a ferrofluid or an MRF/MRE. The value of the coercive field is important for the stability of the system because the magnetostatic attractions between the particles may surpass the electrostatic repulsions of the double layer, thus the lowest remanence possible is preferred [13].

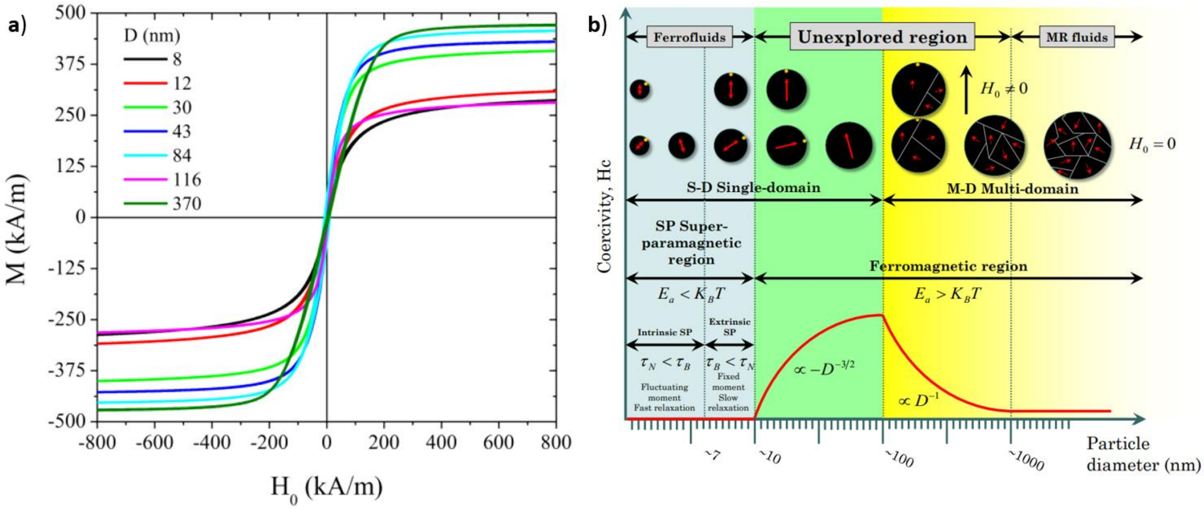

Figure 2.2 a) Magnetic curves for iron particles of various size. b) The effect of the size on the coercivity and the magnetic behaviour of iron particles. Several regions emerge namely the Ferrofluids region where below a critical size the particles display superparamagnetic behaviour due to Neel's relaxation and shortly after thermal rotation. For a second critical size the anisotropy energy surpasses k$_b$*T and the particles obtain a remanent magnetization. The region continues until multiple domains are formed to lower the total magnetic energy and is called unexplored because the particles flocculate. Eventually as the particle's size is further increased, the magnetic domains are too many and have an almost net zero coercivity and at this point the region of the MR fluids begins [3].*

Usually, the magnetic component of the particles is either coated or a part of a composite material to ensure a good affinity with the dispersed phase [14]. Depending on the dispersed phase, polar or non-polar coatings can be applied. A good affinity between the two phases ensures a stable and homogeneous material and without it, the particles aggregate and form clusters [15]. A second reason for the coating is the reduction of the density. The most commonly used magnetic particles (made of iron) have a density around ~7.9 g/cm^3 while the dispersed phase usually has a density near the unity thus, a huge density mismatch exists between these components. As a result, the sedimentation stability can be improved by reducing the overall density through coating of the particle and providing a better affinity with the continuous phase [16]. Lastly, coatings provide functional groups which can be used in certain applications and provide chemical stability in aggressive environments [17]. Unfortunately, the magnetic particles inherit some of the negative effects from the coatings including high cost, complex preparation but more importantly a decline of magnetic properties since the coatings are non-magnetic materials. The decline of the magnetic properties is proportional to the amount of the coating thus thick coatings reduce the Ms by a large amount [18].

Lastly, an important parameter affecting both, the MR performance and the stability of the system is the particles' shape [19, 20]. The mostly common shapes for the magnetic particles include spheres; however, there is a lot of interest for rods as well [21]. Spherical CI particles are produced massively, easily, and cheaply [22]. Rod-like particles on the other hand, have more complex preparations and usually do not have significantly different magnetic properties [23] with the exception of the demagnetization factor. The morphology plays a significant role for MRFs which suffer from the high sedimentation rates [24]. Rod-like particles with a high length over radius ratio have a large free volume which results in thermodynamic repulsions within the suspension, thus reducing the sedimentation rate [7].

2.2 Dispersed Phase

As mentioned before, there are two types of dispersed phases depending if the material is characterized as an MRF or MRE. The particles are suspended in liquids and solid matrices for MRFs and MREs, respectively, thus the prime difference between the two is the viscosity. For the former, the most common liquid phases include silicone and mineral oils; however, different liquids for different applications can be are used. There are two main concerns in regards to MRFs. First the interactions between the particles and the liquid carrier. Bad affinity between the carrier and the particles will result in irreversible large agglomerates which will settle and the suspension will no longer have any uses. Secondly, sedimentation is occurring naturally and many studies were dedicated to either diminish the effect of study it [25]. The sedimentation in a laminar flow was described by Stokes in the following expression:

$$u_s = \frac{2\,R^2 g}{9\,\nu}\,(\frac{\rho_p}{\rho_s} - 1) \qquad 2.1$$

where u_s is the sedimentation velocity, R the radius of the particle, ν the kinematic viscosity, g the gravitational acceleration, ρ_p the density of the particles, and, ρ_s the density of the solvent. The sedimentation velocity is inversely proportional to the viscosity of the liquid carrier and it is impacted by the density mismatch of the system. It is obvious that it is easier to fight sedimentation using carriers with higher viscosity. Unfortunately, the viscosity of the carrier also affects the MR performance of the material. When a magnetic field is applied the particles within the suspension form chain-like structures which transform the suspension in a soft yield stress fluid. The viscosity of the carrier acts as a hinderance for the chains with its effect already well established [26]. So, a high viscosity hinders both the sedimentation and the magnetic response of the material thus the liquid carrier should be selected accordingly.

An obvious advantage of the MREs is the solid polymeric matrix in which the particles are embedded. Thus, sedimentation is not an issue however, the MR effect is significantly smaller when compared to MRFs which is not a big issue as MREs have their own unique applications. Due to the enormous advances in the polymer sciences, there are countless potential properties that MREs may inherit, thus vastly changing the type of the application from polymer to polymer. The most common types of polymeric matrices include the following. Silicon rubber is a great candidate as it can be ordered at various molecular weights thus, controlling the materials viscosity/elasticity. Additionally, this rubber is usually in a liquid state which allows the particles to be well distributed during preparation. Lastly, if cured under the presence of a magnetic field, the chain-like structures that the magnetic particles form will be permanent, an attribute that MRFs do not have [27]. Thermoplastic elastomers allow the reprocessing of the MRE allowing them to be recycled without losing their MR properties [28]. Lastly, the dispersed phase can be a two-component system thus it is important to include MR materials like MR foams and MR gels which have their own unique properties and uses [29]. There are several other types of polymeric matrices with genius applications however, it is out of the scope of this thesis. Similarly, both MREs and MRFs may include different types of additives which improve the materials however, these are not part of the investigation for this thesis.

2.3 Magnetorheological Effect

The MR effect was described as the alignment of the particles when an external magnetic field is applied which is shown in **Fig. 2.3**. Assuming there are no other forces and the medium is non-magnetic, during the off-state, the particles are randomly dispersed. When a magnetic field is applied, the particles become magnetized. Assuming that the particles act as single dipoles and (a fairly accurate approximation), the state with the lowest energy is achieved when the particles organize themselves into chains which are as far away as possible given the simple dipole potential energy:

$$U = -\vec{m} \cdot \vec{H} \qquad 2.2$$

with $\vec{m}$ and $\vec{H}$, being the magnetization of a single dipole and the magnetic field imposed from an external magnetic field (which can be considered as a neighboring dipole), respectively.

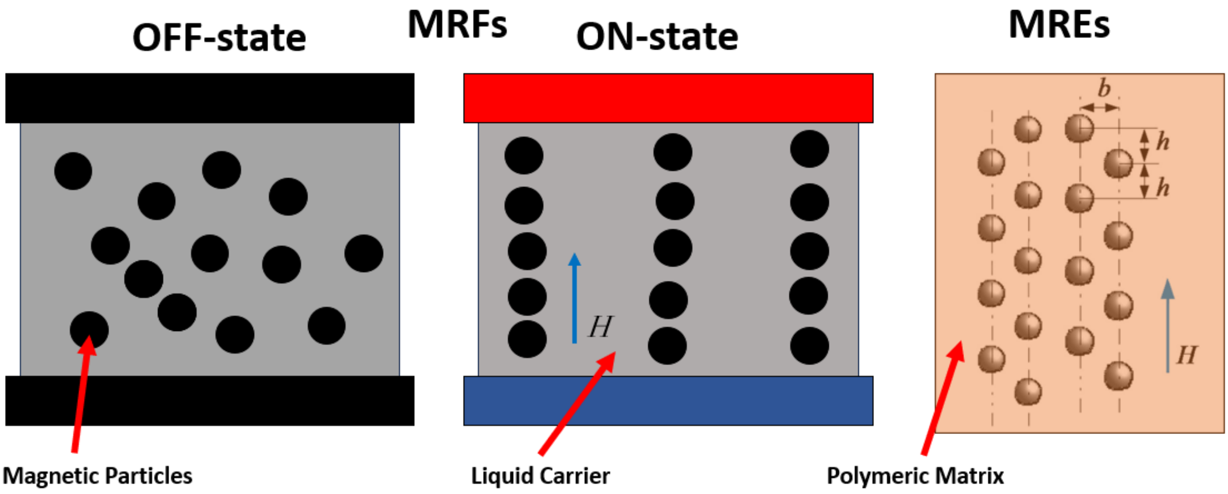

Figure 2.3 Schematic illustration of the MR mechanism for MRFs in chain-like structures and for MREs as suggested from Han et al [30]

This mechanism is very accurate for the liquid carriers whose viscosity values are low, thus mainly MRFs. For materials with a higher viscosity the particles cannot move (as) freely within the medium and are locked in place. This is the case for MREs which still possess an MR effect, however, a different mechanism is suggested. In this case the particles are also considered small enough to be considered as magnetic moments and all of them are considered to share the same magnetization. Then the interaction energy for 2 dipoles can be written as:

$$U = \frac{\mu_0 m^2}{4\pi r^3}(1 - 3cos^2\theta) \tag{2.3}$$

where μ_0, r and θ are the permeability of free space, the distance between the moments, and their angle, respectively. Again, the energy takes its lowest value when the moments are parallel in chain-like structures. By defining a shear strain, it is possible to show that a positive MR effect takes place through the derivatives of the interaction energy [31]. However, for a uniaxial deformation the opposite is true. Experimentally, MREs experience a positive MR effect during uniaxial deformation thus it was proposed that the particles obtain wavy configurations which topologically is closer to the reality as can be seen in **Fig. 2.3** [30].

Lastly, a different kind of MR effect which is not often mentioned is the change in electrical properties of the material. For MRFs, during the on-state, the formation of chain-like structures allows for conductive pathway to be formed. The carriers can move more efficiently thus increasing the conductivity of the system. It is suggested that the carrier transport is achieved via both variable-range hopping mechanism or the correlated barrier hopping [32]. Similar to the mechanical properties, the conductivity is less affected in MREs. The particles are not aligning thus the barrier is higher for the charges to overcome. For anisotropic MREs on the other hand, the particles are aligned during curing and remain with the chain-like structure even during the off-state. For these MREs the conductivity is increased as well due to the magnetostriction phenomenon which reduces the distance between particles thus reducing the barrier for the charge carriers to bypass which increases the conductivity [33].

2.4 Rheology of MR systems

Rheology is a powerful tool to describe, characterize, and analyze MR systems. Magnetorheological systems usually display a complex behaviour which needs to be decoded in order to understand and determine if the given sample is appropriate for a specific application.

2.4.1 Rheology of MRFs

Magnetorheological fluids can be investigated using both rotation and oscillation modes; however,1 this thesis is focusing mainly in rotational rheology as it is the most common type of operational mode in applications [34]. In these experiments, a rotational deformation is imposed to the sample and the stress is measured by rheometer for a given shear rate. The most typical characterization test is the measurement of stress for increasing shear rates which is commonly known as a flow curve. The dynamic viscosity (henceforth always referred to as viscosity) is defined as the ratio of the shear stress over the shear rate. For fluids 4 typical behaviours are shown in **Fig. 2.4**. For the Newtonian behaviour, the viscosity remains constant and independent of the shear rate. For shear thinning and shear thickening behaviour on the other hand, the viscosity decreases or increases respectively with increasing shear rate. Magnetorheological fluids with all of these behaviours have been reported [21]. Lastly, materials that require a certain load to flow (Bingham plastic in **Fig. 2.4**, such as toothpaste, are important as this type of behaviour resembles well MRFs during the on-state. A typical flow curve for an MRF is shown in **Fig. 2.5a**. During the off-state a given suspension with a low concentration of magnetic particles φ displays a Newtonian behaviour. When an external magnetic field is applied the particles form chain-like structures and as a result the stress is increased and the behaviour changes to that of a yield stress fluid. Higher fields result to more robust chains, thus higher yield stresses (τ_y). Once the particles are magnetically saturated, the yield stress does not increase anymore. At lower shear rates the magnetostatic interactions dominate. At some point, as the shear rate is increased, the hydrodynamic forces will become relevant and a short transition region is observed. Before long, the hydrodynamic forces will surpass the magnetic and chains will be disrupted leading back to a

Newtonian behaviour or an overall Bingham plastic. The yield stress dependence on the external magnetic field is divided in three different power laws depending on its strength and is displayed in **Fig. 2.5b**. At small fields, the yield stress is proportional to the strength of the magnetic squared.

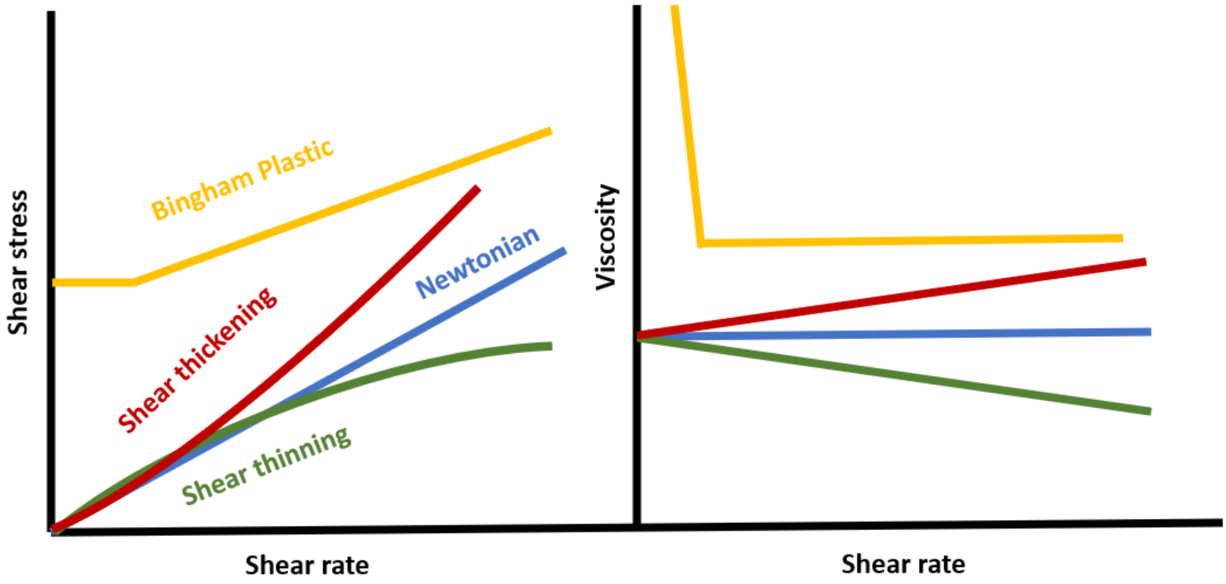

Figure 2.4 Typical flow profiles for various types of fluids.

When saturation begins the power law is $\tau_y \sim M_s^{0.5} H^{1.5}$ and eventually for larger magnetic fields $\tau_y \sim M_s^2$, with M_s being the saturation magnetization of the particles [35]. The yield stress depends on the particle concentration and at low φ the dependence is linear. At some point the power law becomes greater than unity [36]. Then there is an increase in viscosity and that is due to increase of the yield strength, this increase can be many orders of magnitude. This behavior is commonly known as the Bingham model and it is shown by the following equation:

$$\tau = \tau_y + \mu\dot{\gamma} \qquad 2.4$$

Where μ, and $\dot{\gamma}$ are constant with viscosity units, and the shear rate, respectively. Note that when the hydrodynamic forces take over, the behaviour can be non-Newtonian where other models for yield stress materials can be used such as the Herschel Bulkley, De Kee and more [37]. Other parameters that influence the flow curves include the temperature, the pressure, the polydispersity and the morphology which this thesis is more concern about. It is important to note that MRFs whose magnetic forces operate over a broad shear rate range are appreciated the most.

In the field of magnetorheology, the ration of the hydrodynamic forces over the magnetic ones is both a very important and a known quantity named Mason number (Mn) which is given by the following expression [26]:

$$Mn = \frac{9\, n_m \dot{\gamma} \varphi}{2\mu_o \mu_m M_m^2} \qquad 2.5$$

where n_m the dynamic viscosity of the continuous phase, μ_0 the permeability of the free space, μ_m the permeability of the continuous phase, and, M_m the magnetization of the suspension.

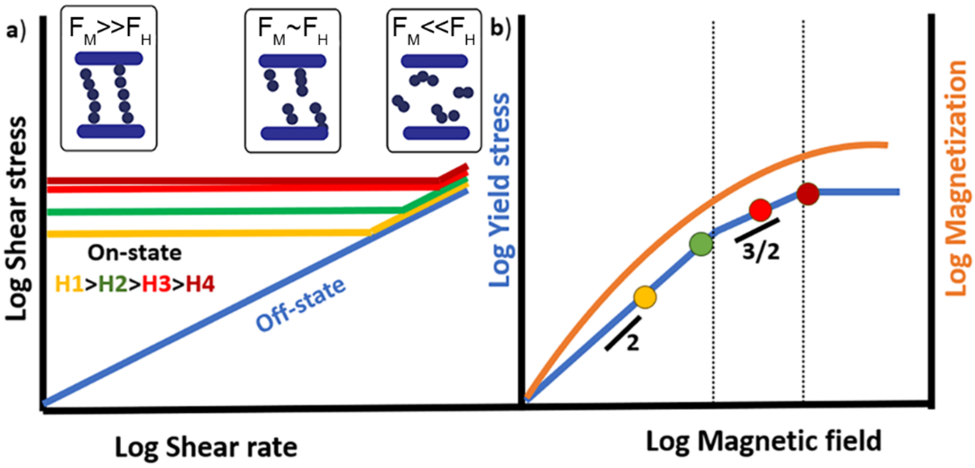

Figure 2.5 a) Typical flow curves for a hypothetical MRF during the on- and off-state together with an illustration of the fluid's structure. b) The yield stress and magnetization dependency on the magnetic field in blue and orange respectively for the same hypothetical MRF. The slopes are indicating the yield stress dependency and coloured circles the yield stress from part a).

Basically, a high *Mn* corresponds to the domination of the hydrodynamic forces. As can be seen in **Fig. 2.6a** the viscosity drops with a constant rate until a critical *Mn** is reached where the hydrodynamic forces are of the same order as the magnetic ones. Shortly after, hydrodynamic forces dominate reaching the high shear rate plateau. The *Mn* allows the data to be plotted in a single mastercurve with an example shown in **Fig. 2.6b** and as can be seen, since *Mn* is always <<1, the magnetic contribution dominates. It must be noted that all of the Eq 2.5 components are either known or can be estimated precisely from a single magnetic curve of the magnetic particles given the viscosity of the carrier is also known (usually provided from the supplier). So, using the *Mn*, it is easy to predict the MR behaviour of an MRF for a broad range of concentrations without performing any experiments which saves time and resources thus highly appreciated by the industry.

Other important numbers include the λ parameter which is the ration between the magnetic and thermal forces:

$$\lambda = \frac{\pi \mu_o \mu_m b^2 R^3 H^2}{2 k_b T} \qquad 2.6$$

where k_b, T, and, b are the Boltzmann's constant, the absolute temperature, and, the magnetic coupling parameter respectively. At saturated fields λ scales with M_m instead. The systems used in this thesis have relatively large R and H thus it is assumed that $\lambda >> 1$. The λ parameter is connected with the Mn though the Peclet number $Pe = 1.5Mn\lambda$ [35].

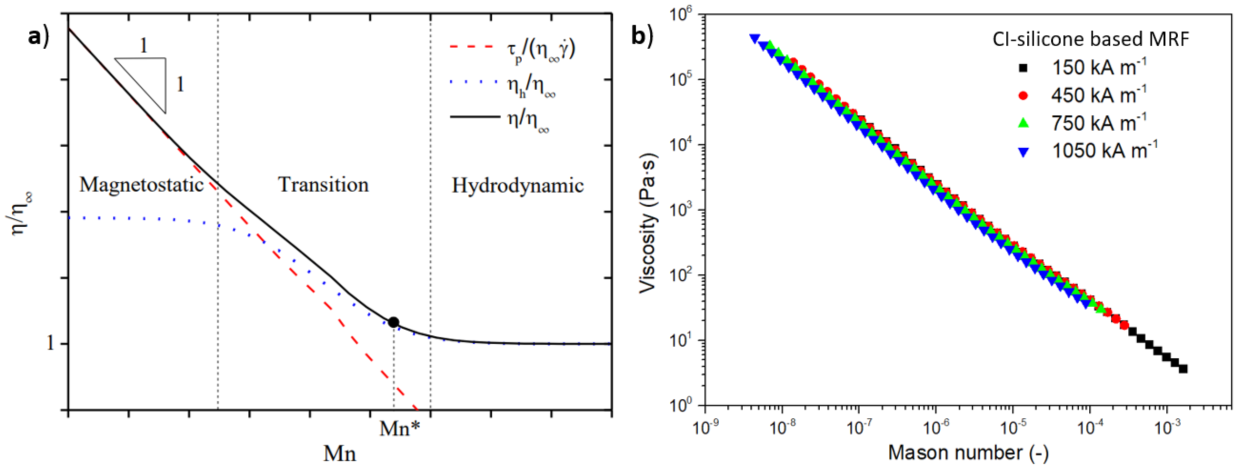

Figure 2.6 a) Apparent viscosity as a function of Mn. The red and blue dotted line represent the magnetic and hydrodynamic contributions to the viscosity and the black line is the overall behaviour. [38] b) An example of a mastercurve for a standard CI based MRF [7].

Lastly, the most important ration not discussed yet is the MR effect which essentially describes the performance of the MRF at a specific magnetic field value and shear rate. To be specific the MR effect is defined as the ration between the on-state stress or viscosity over the corresponding off-state value. For oscillatory tests instead of complex viscosity, usually the storage modulus *G'* is used to calculate the MR effect in a similar to the rotational rheology way. More precisely the MR effect for the rotational and oscillatory modes is defined in the following equations:

$$e_r = \frac{\tau_{on}}{\tau_{off}} = \frac{n_{on}}{n_{off}}, \tag{2.7}$$

$$e_s = \frac{G'_{on}}{G'_{off}} \tag{2.8}$$

2.4.2 Rheology of MREs

There are various applications in which MREs are used in oscillatory mode such as dampers and shock absorbers [39]. An efficient way to investigate the viscoelastic properties of a material is achieved through oscillatory tests. In these experiments, an oscillatory deformation is applied to the sample at a given frequency and the stress is measured by rheometer. The regime where the stress and strain have a linear relationship at any frequency is called linear viscoelastic regime. The stress response is sinusoidal which usually has a phase lag compared to the imposed strain. A completely elastic material is in phase with the strain. On the other hand, a completely viscous material has a 90° phase angle difference. A viscoelastic material shows a response between elastic and viscous and hence the phase angle (δ) is between 0–90° which is usually the case for MREs. The phase angle holds the viscoelastic information, from the imposed strain and the measured stress.

The viscoelastic information can be extracted from the complex modulus $G*$ and the phase angle which allows the separation of $G*$ into a real and an imaginary part. The real part (G') is the storage modulus or elastic modulus which represents the stored deformation energy and it is usually associated with the MR effect. The imaginary part (G'') is the loss modulus which represents the tendency to dissipate energy thus very important in the damping applications of the MREs. The phase angle may take values of 0° and 90° responding to purely elastic and viscous behavior, respectively, whereas intermediate values correspond to a viscoelastic behavior. Materials with higher G' than G'' are said to display a solid-like behaviour. Likewise, if the G'' is considerably higher the materials experience a liquid-like behaviour. The equations which connect these parameters are:

$$G^* = (G'^2 + G"^2)^{1/2} \qquad 2.9$$

$$G' = G^* \cos(\delta) \qquad 2.10$$

$$G^" = G^* \sin(\delta) \qquad 2.11$$

$$\tan(\delta) = \frac{G"}{G'} \qquad 2.12$$

Several types of oscillatory tests can be used to investigate the behavior of MREs materials with the most common discussed in detail below.

Dynamic Strain Sweep (DSS) tests describe the deformation behavior of a material, these tests are mainly used to investigate the limit of the applied deformation in which the inner structure of the material remains unaffected. For a given temperature, an oscillatory deformation is applied at a constant frequency for varying strain amplitudes and the G' and G'' at each strain are calculated. The linear viscoelastic regime (LVE) is defined as the range of strain at which the storage modulus G' becomes strain independent. The critical strain γ_L (the onset of non-linearity) in **Fig. 2.7a** indicates the limit of the LVE at the point where the plateau of *G’* starts to drop. In the LVE, tests can be carried out without destroying the material’s internal structure. For MREs specifically these measurements are more complex as these are usually highly filled polymers, thus subject to the Payne effect [40]. The signature of the effect is a sudden shoulder of the *G”* towards the end of the LVE as can be seen in **Fig. 2.7b**. Applying a magnetic field usually shifts the values of the *G’* to higher values without changing the trend of the overall behaviour.

Dynamic Time Sweep (DTS) tests are mainly used in curing studies and are also useful to observe solvent evaporation or drying. Additionally, these tests can detect the thermal degradation of the sample and crosslinking which is relevant to this thesis [41].

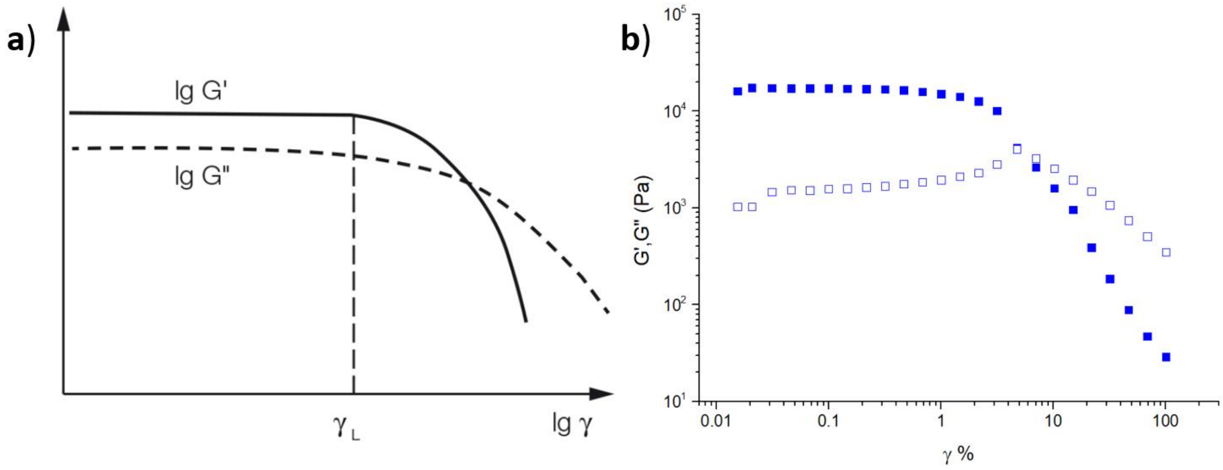

Figure 2.7 a) Typical DSS for a polymeric system. The plateau of G’ indicates the linear regime with γ_L *being the limit of linearity [41]. b) DSS for a carbon black based elastomer, closed and open symbols correspond to G’ and G”, respectively.*

These tests have been used to study MREs with time-dependent behaviour, for instance, systems where the particles and the host matrix interact. Potential changes in the viscoelasticity are detected over time while the material undergoes an oscillatory deformation at a constant strain and frequency. In this thesis, DTS tests are used to secure that the sample has reached steady state when the samples were loaded at high temperatures. This is indicated when *G’* and *G”* are not changing with time as shown **Fig. 2.8** where after ~6 minutes the sample reached a steady state however, it can take much longer even several days.

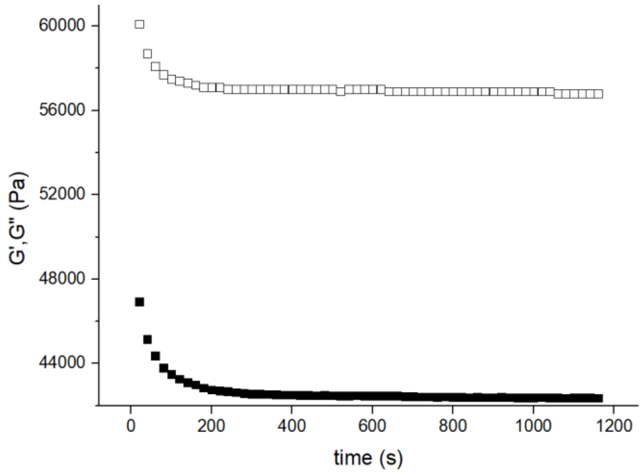

Figure 2.8 DTS for a CI/thermoplastic-based MRE right after loading at 170 °C. Closed and open symbols correspond to G' and G", respectively.

Dynamic Frequency Sweep (DFS) tests describe the viscoelastic spectra of a material. Repeating these tests for different temperatures, characteristics like the melting point, glass transition, rubbery plateau, relaxation times, phase transitions and more can be studied [42]. The strain amplitude is kept constant and the frequency is varied. The shape of *G'* and *G"* over frequency can characterize the material's structure. A common example for linear polybutadiene with entanglements is shown in **Fig. 2.9**. The viscoelastic spectrum is shown in four regions corresponding to different characteristic sizes and a characteristic relaxation time for each size can be extracted. For the glassy region at high frequencies or short times (or low temperatures), the behavior is solid-like with modulus being time independent. Such short times correspond to the chemical bonds and the molecules are shown seem "frozen" as the frequency is higher that their movement. Giving more time for the molecules to start moving, the modulus drops as local parts of the chains start to relax. As the time passes, larger parts relax further reducing the moduli until the chains are completely relaxed and the material is flowing. However, usually the molecular weight of the polymer is large enough and there are entanglements in which case a plateau is formed just like in **Fig. 2.9**. The time needed for the chains to completely relax depends on the molecular weight and when the terminal regime is reached, the Maxwel behaviour with a characteristic drop of the moduli can be observed, indicated with the slopes of 1 for *G"* and 2 for *G'* in a log scale as shown in **Fig. 2.9**. For MREs the two regions at low frequencies are important since above the T_g the chains are frozen and so are the particles, thus no MR effect can be displayed.

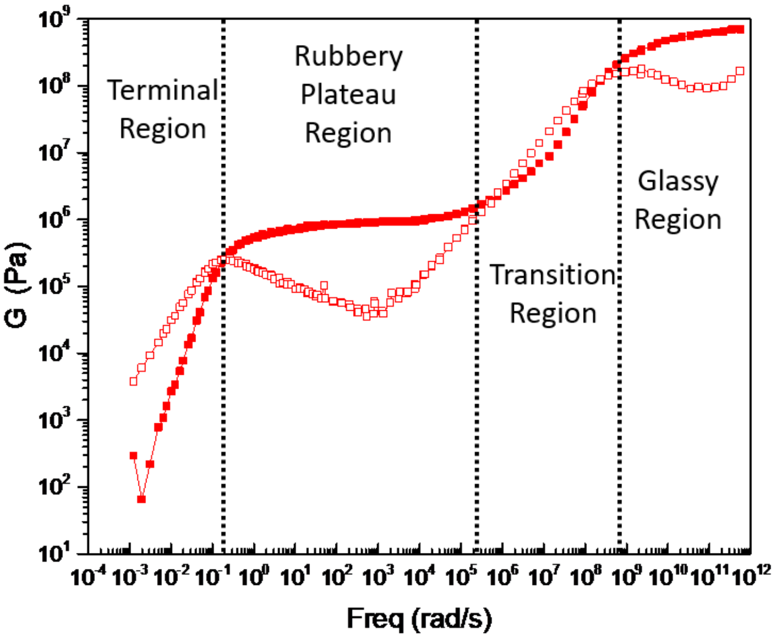

Figure 2.9 Viscoelastic moduli G' and G" (closed and opened symbols, respectively, for a linear polybutadiene with Mw = 155 Kg/mol at 250 K. The data were kindly provided by Leo Gury.

Adding the magnetic particles to the pure polymer will shift the rubbery plateau to a higher modulus. The value of the rubbery plateau for the pure polymer is important to know as the MR effect for a given particle concentration can be calculated relevantly accurately [31]. The terminal regime is also very important as MREs which just like filled elastomers do not display the Maxwell behaviour. Instead, *G'* and *G"* either drop with different slopes or even display a secondary plateau. To conclude, DFS graphs and their derivatives may give great insight of the material's structures and are a powerful tool to characterize an MRE.

3. MOTIVATION AND AIMS OF THE THESIS

3.1 Motivation

Progress in MRFs by the Juan de Vicente, Daniel J. Klingenberg and Jose R. Morillas were the inspiration to study the topic of this thesis due to their creativity and dedication to the field [11, 26, 35, 43-46]. The field of magnetorheology has many advances in both fundamental research and applications. However, in the author's opinion there is a big gap separating these advances. For example, fundamental research uses perfect homogeneous fields which are unlikely to be achieved in applications. On the contrary, the flow and deformations in real applications are not considered in fundamental research. Works that will marry fundamental research with the applications for both MRFs and MREs is the main motivation of this thesis.

3.2 Aims

Aims of this study include:

- Study of polypyrrole-based MRFs
- Study the impact of magnetic tubes in conventional MRFs
- Fabrication and study of electronic devices based on various MRFs
- Fabrication of recyclable MREs
- Study the particle-matrix interaction within MREs

4. SELECTED RESULTS

4.1 Polypyrrole nanotubes-based MRFs

In this thesis 2 types of magnetic particles are used. First, conventional CI particles supplied by BASF (Germany) and secondly, polypyrrole (PPy) based magnetic nanotubes which were synthesized [7]. The PPy nanotubes were synthesised and decorated with magnetite nanoparticles during a two-step synthesis. Two samples were synthesized at different molarities of iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$). **Table 4.1** presents the amount of each component used with the mole ratio of $FeCl_3 \cdot 6H_2O$ over pyrrole represented as n. For the synthesis, firstly the pyrrole (>97%) was dispersed in water (0.2 M in 100 mL) with methyl orange (0.004 M in 100 mL) being added later on. The dye is the key substance which guides the growth of tube-like morphology instead of spheres. Aside, a second solution of $FeCl_3 \cdot 6H_2O$ in water ($FeCl_3 \cdot 6H_2O$ is 0.5 M in 100 mL for n=2.5 and 1.2 M in 100 mL for n=6) was prepared. Right after, both solutions were combined and the polymerization of pyrrole to the PPy nanotubes was complete at room temperature once the mixture turned dark brown/black and thickened with the procedure taking a few minutes. **Fig. 4.1** shows the main synthesis reactions. The final molar concentrations of the reaction mixture are: 0.1 M pyrrole; 0.25 M $FeCl_3 \cdot 6H_2O$ – for n=2.5 and 0.6 M for n=6 and 0.002 M methyl orange. To decorate the PPy nanotubes with magnetite, the resulting PPy dispersion was mixed with an excessive amount of ammonium hydroxide (4 M) at room temperature until the solution became basic (pH > 10). Lastly, the decorated nanotubes were isolated by filtration and washed with ethanol. The particles were left to dry overnight at 60 °C.

Table 4.1. Preparation compositions for PPy/magnetite nanotubes.

	n	Pyrrole (mL)	$FeCl_3 \cdot 6H_2O$ (g)	Water (mL)	Methyl orange (mg)
PPy2.5	2.5	1.4	13.52	200	130
PPy6	6	1.4	32.45	200	130

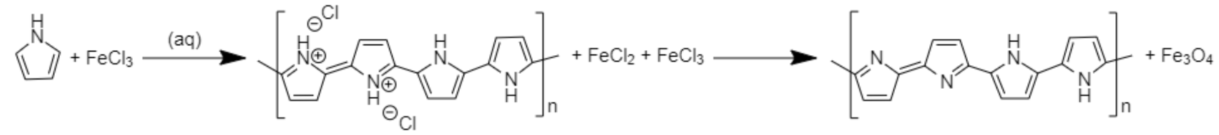

Figure 4.1 The two-step synthesis of magnetic nanotubes; PPy nanotubes are first created using the oxidation of the pyrrole with $FeCl_3·6H_2O$. Excess amounts of $FeCl_3·6H_2O$ lead to the creation of magnetite under alkaline conditions converting PPy to a base [7].

4.2 MRF-based electronic devices

Electrical devices with tunable parameters that utilize MRFs are on the rise [47]. Such a device was fabricated based on the PPy2.5 and PPy6 magnetic tubes which were dispersed in silicone oil with a volume concentration of 50 %. In short, several MRFs based on these particles and silicone oil were prepared. The device basically consists of an MRF that is sandwiched between two copper plates as shown and described in **Fig. 4.2a, b** in detail. The device is the connected with an RLC bridge and is placed inside a set-up that may impose static magnetic fields as shown and described in **Fig. 4.2 c**.

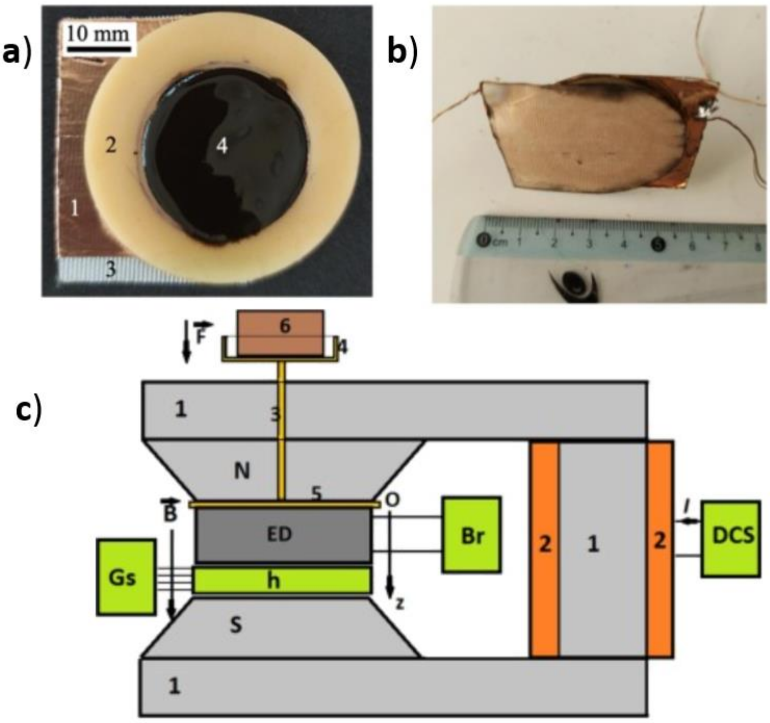

Figure 4.2 a) Top view of the electric device (ED) with 1 being the copper plate, 2 a natural rubber ring with diameter and thickness of 20 and 2 mm respectively, 3 is an insulating tape and 4 the MRF. b) The ED covered with the copper plates from both sides. c) The measuring set-up with 1 being the magnetic core, 2 copper coils connected to a DC source (DCS) for the production a magnetic field, 3-5 base for a load, 6 being an 800g load. The ED is connected to a power source (Br) [15].

It is possible to use a superimposed AC signal together with any combination of a static electric and magnetic fields. The MRF-based device acts as a capacitor with an equivalent resistance connected in parallel. The electrical properties of the MRF-based device can be measured under various conditions. When a static external electric field is applied, the particles can become electrically polarized and the whole MRF improves its dielectric properties. The distance of the dipoles is basically the distance between particles when the chain-like structure is formed. It is possible to alter this distance by varying the electric and magnetic fields, thus control the properties of the dielectric as a whole. The mechanism and how the external fields affect the interparticle distance is presented in **Fig. 4.3** in detail.

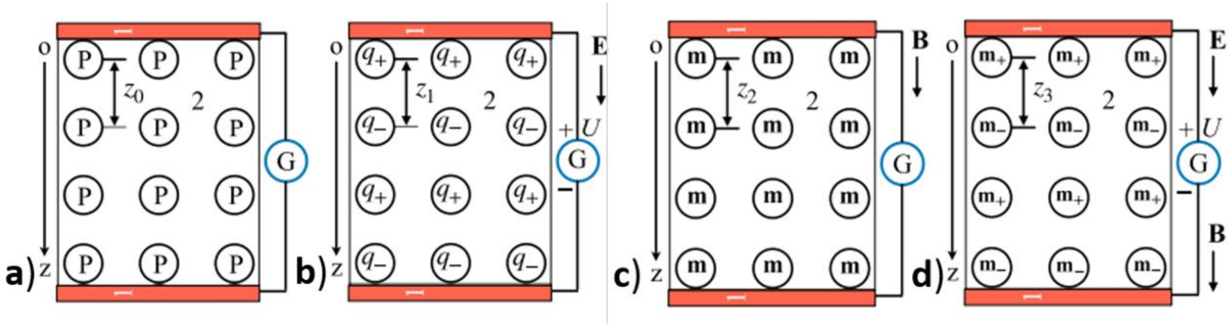

Figure 4.3 The MRF-based electric device under various conditions. a) No electric or magnetic fields are applied; the particles are considered to be randomly dispersed with an average distance between them z_0*. b) Only an electric field is applied, the particles become electrically polarized and form column-like structures with an average distance between particles being* z_1*. c) Only an external magnetic field is applied and the particles are magnetically polarized with an average distance between them* z_2*. d) Simultaneous application of an electric and magnetic field. The average distance is now* z_3 *which is the shortest [48].*

Fig. 4.4 displays the dependance of the equivalent resistance and capacitance for the same MRF, based on PPy6 particles at different frequencies and loads (a,b 1 Hz, 900 g, c,d 10 Hz, 800 g, constant impedance). For all samples the resistance has a decreasing tendency both with electric and magnetic fields. The resistance drops at a specific rate denoted by the fitted curves in **Fig. 4.4a**. The slope is independent of the magnetic field. In the given experimental window, the magnetic field has a higher impact for both samples when compared with the influence of the electric field with the resistance being half, at saturated fields. The capacitance has different trends. For the sample tested at 1 Hz **Fig. 4.4b**, the capacitance has a strong response both with the electric and magnetic fields. Unlike the resistance, the impact of the magnetic field depends on the electric field. For the sample measured at 10 Hz, the capacitance shows a completely different trend when compared to the 1Hz sample. The electric field is not particularly impactful and a good response is only observed when the magnetic field is altered. As can be seen by varying certain parameters, it is possible not only to tune the electrical properties of these MRF-based devices but to obtain different trends. There are three extensive studies based on these MRF-based electrical devices with all the details [15, 48, 49].

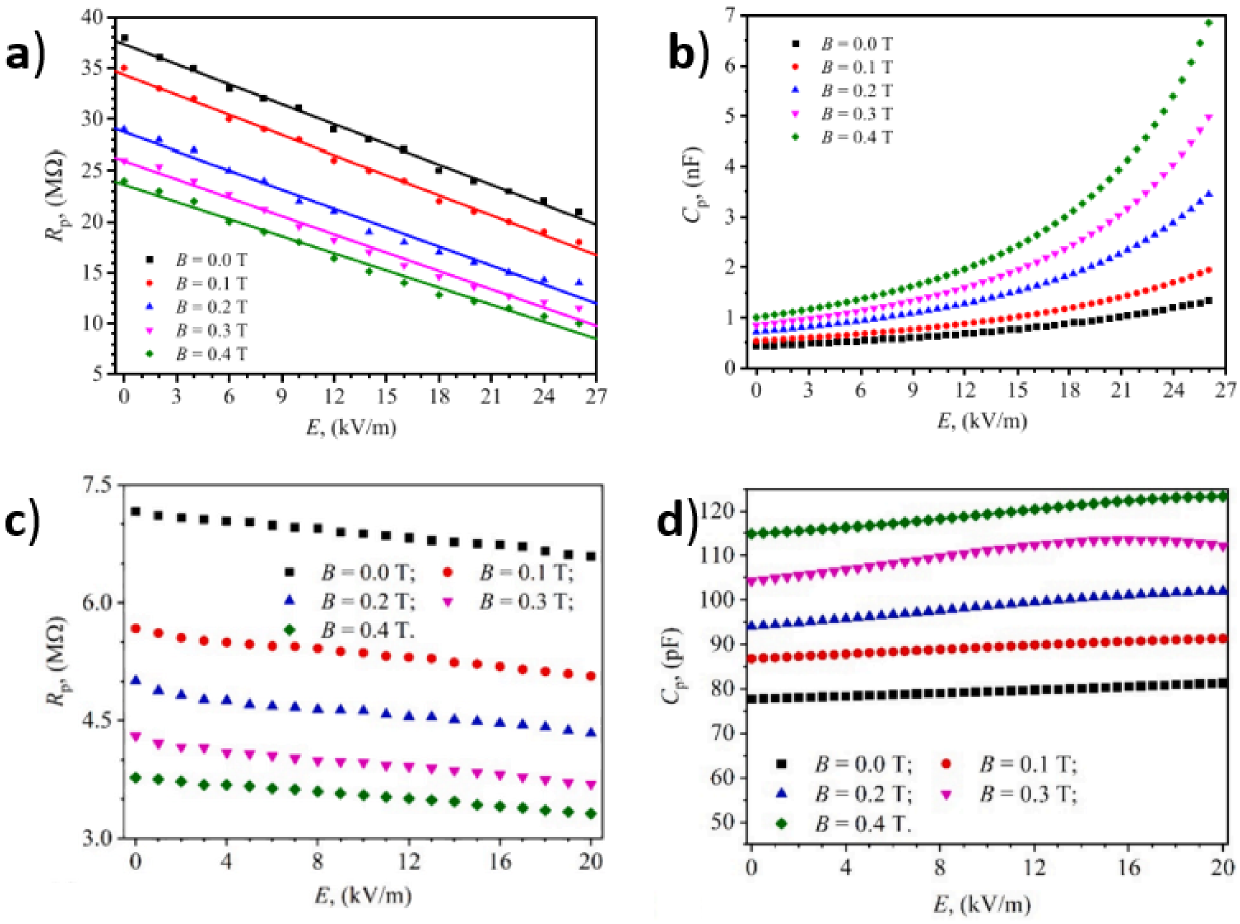

Figure 4.2 Capacitance and its equivalent resistance for an electric device at a,b) 1 Hz and 900 g load, and c,d) 10 Hz, 800 g load and constant impedance of 100 kΩ at the terminals of the RLC meter [15, 48].

4.3 Dimorphic MRFs

A dimorphic magnetorheological fluid (DMRF) is usually a three-component system composed of a conventional MRF and another type of magnetic or non-magnetic particles with a different morphology. For example, spherical and rod-like particles dispersed in an oil. There are only a handful of publications that include dimorphic MRFs, thus there is a large gap in the field to investigate [50, 51]. Moreover, to our knowledge, DMRFs based on magnetic nanotubes were not studied. Two different DMRFs were prepared with the characteristics presented in **Table 4.2**.

The MR effect of the samples at low and saturated fields is presented in **Fig. 4.5**. For both graphs the MRF 2.5 has overall inferior performance except at high frequencies in **Fig. 4.5a**. The MRF 6 on the other hand, shows similar performance to the conventional MRF at saturated fields. However, at low fields, the MRF 6 outperforms the standard MRF by a considerable amount. The reason behind this observation was deemed to be the different types of magnetic particles. Despite having a much lower *Ms*, magnetite saturates at lower fields as was shown in **Fig. 2.1**.

Table 4.2 Composition of the prepared magnetorheological fluids in vol%.

	Code name		
Components	MRF 2.5	MRF 6	Standard MRF
Carbonyl iron	10	10	10
PPy2.5	1	0	0
PPy6	0	1	0
Silicone oil	89	89	90

Thus, the chain-like structures formed at the lower fields are more robust giving rise to a better MR effect. This is very important as less powerful fields are required to reach a better MR effect, thus less energy consumption is needed.

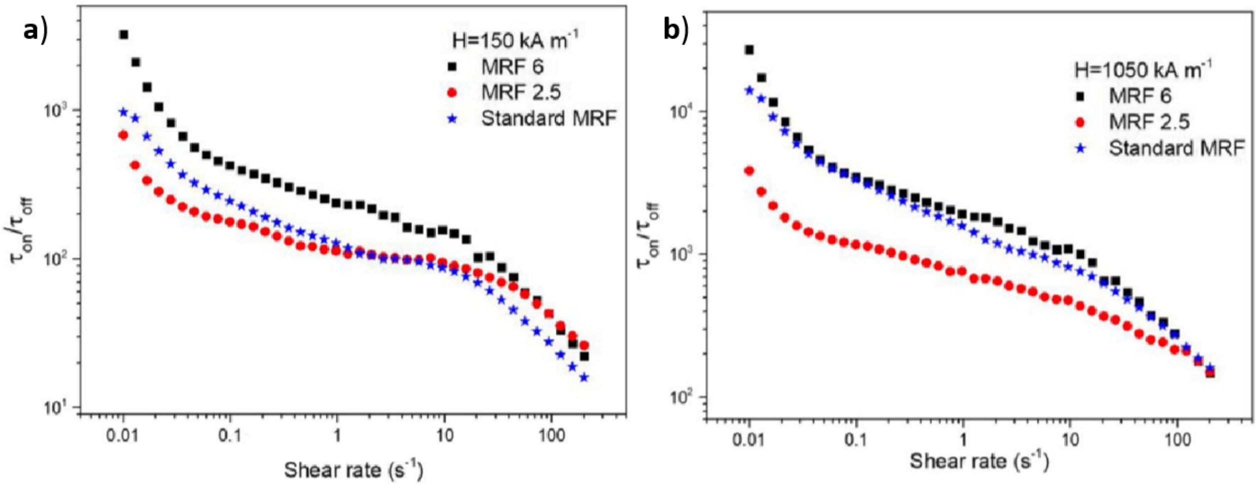

Figure 4.5 MR effect of various DMRFs compared to a standard MRF at different shear rates and magnetic fields a) 150 kA/m, b) 1050 kA/m [7].

The DMRFs were also tested at elevated temperatures through step-wise test with the MRF 6 sample shown in **Fig. 4.6a**. To be precise, the samples were subjected to a steady shear and the magnetic field was turn on and off repetitively with the field being constantly increasing between steps. At 60 °C the chains remain robust and the on-state shear stress is only slightly reduced when compared with the shear stress at room temperature. However, during the off-state the viscosity is more temperature dependent which leads to a considerably lower shear stress. The average of all shear stress points at a given period is used to calculate the MR effect in **Fig. 4.6b** where all samples are compared. Key findings include that the MR performance is affected by the temperature especially at saturated fields. The DMRFs have much higher MR effects when compared to the standard MRF which is very impressive as only 1 vol% of nanotubes was added. The study includes the investigation of the effect of the nanotubes on the sedimentation stability, *Mn* and other key properties for magnetorheology [7].

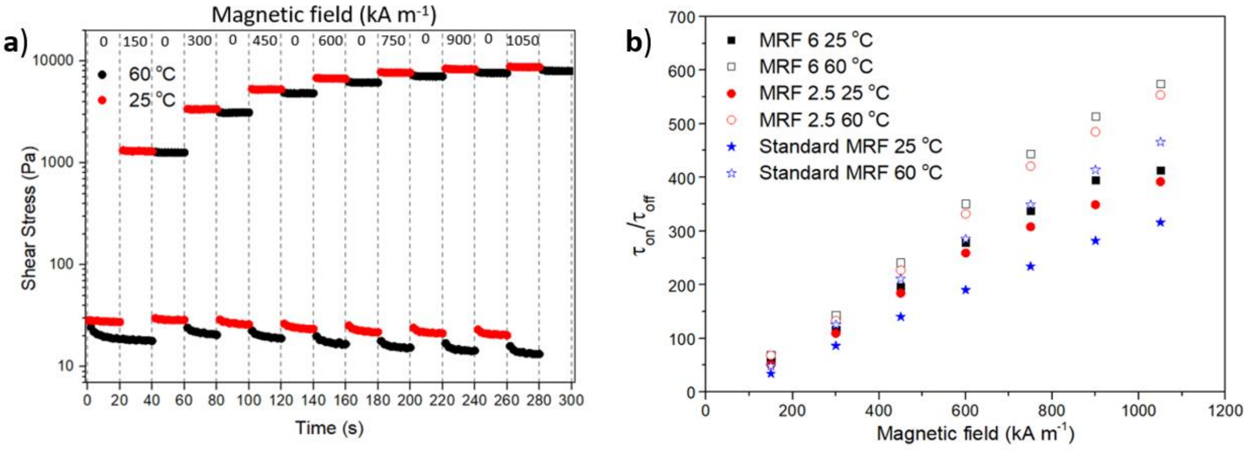

Figure 4.6 a) Effect of the step-wise increase of the magnetic field on the shear stress under a steady shear of 50 s^{-1} at different temperatures for the MRF 6. Changes of the magnetic field are illustrated with dotted lines with the values noted on top. The sample at 25 °C is shifted by 20 seconds for clarity reasons. b) MR effect at different magnetic fields for different MRFs at room temperature and 60 °C [7].

4.4 Recyclable MREs

One of the most commonly used matrices in MREs is silicon rubber due to its liquid state in which the magnetic particles can be dispersed homogeneously before curing. However, such elastomers cannot be recycled. In this section the possibility of reprocessing of MREs is showcased. The matrices are prepared through compression moulding using a polyurethane-based thermoplastic elastomer and CI particles, at different concentration, which are mixed prior inside a compounder. The samples were used in various tests, then they were recycled and tested again with this process being repeated three times with all the details included in the published paper [52]. As can be seen in **Fig. 4.7**, results show that in terms of mechanical properties both of the MREs and the pure elastomer managed to keep overall the same properties even after three reprocessing cycles. The tensile strength and the elongation at break are slightly reduced for every cycle; however, considering that in applications usually only one third of recycled material is used, these are very satisfying results. Only the after being recycled three times (R3), the reprocessed MRE sample started to show noticeable changes. On the other hand, as shown in **Fig 4.7b**, the values of the Young's modulus were only sustained for the pure elastomer with the MRE showing a degrading trend with each reprocessing cycle.

The magnetorheological properties of these samples were also examined. For samples with a low content of CI particles, no MR effect was observed as the elastomer is too stiff for the particle to move.

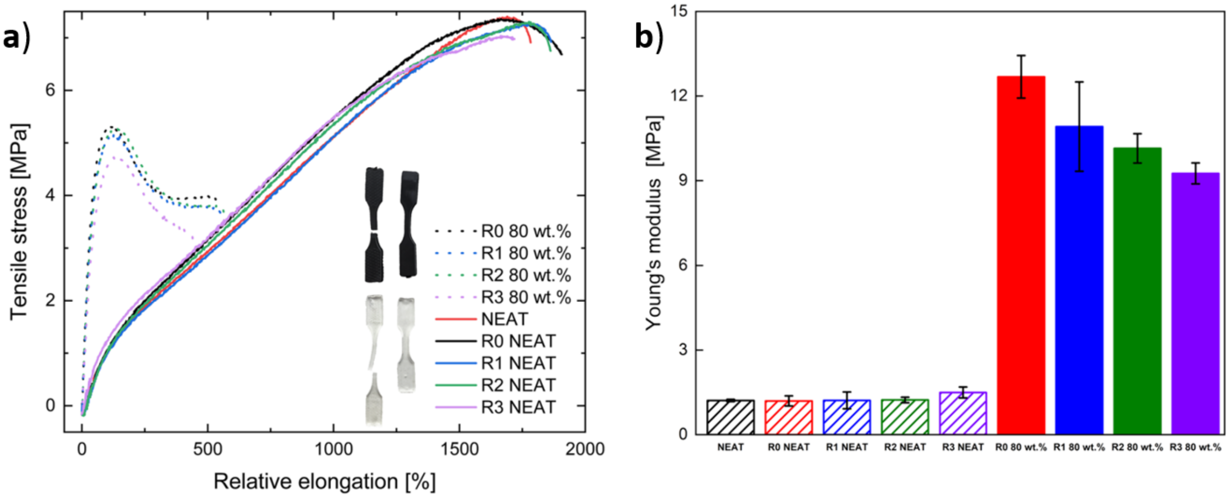

Figure 4.3 a) Tensile tests for a reprocessed thermoplastic MRE with 80 wt% filling and their pure analogs. b) the Young's modulus of the same samples. R0-R3 indicate the preprocessing cycle i.e. R0 the first sample, R1 once reprocessed sample etc. [52].

For the 80 wt% MREs, there was also no MR effect with the reasons explained in detail in the following **section 4.5**. Only for samples with a 50 wt% filling an MRE effect was observed and only for the non-reprocessed ones. This is demonstrated through dynamic strain sweeps in **Fig. 4.8a** where the *G'* increases with increasing magnetic fields within the LVE. The MR effect of the corresponding samples is shown in **Fig. 4.8b** and it must be noted that it is defined as the ratio of the difference between the *G'* of the on- and off-state over the *G'* of the off-state thus it is expected to be much lower than the one defined from **Eq. 2.8**. The reprocessed MRE displays a typical dependence on the magnetic field as described in the **section 2.4**.

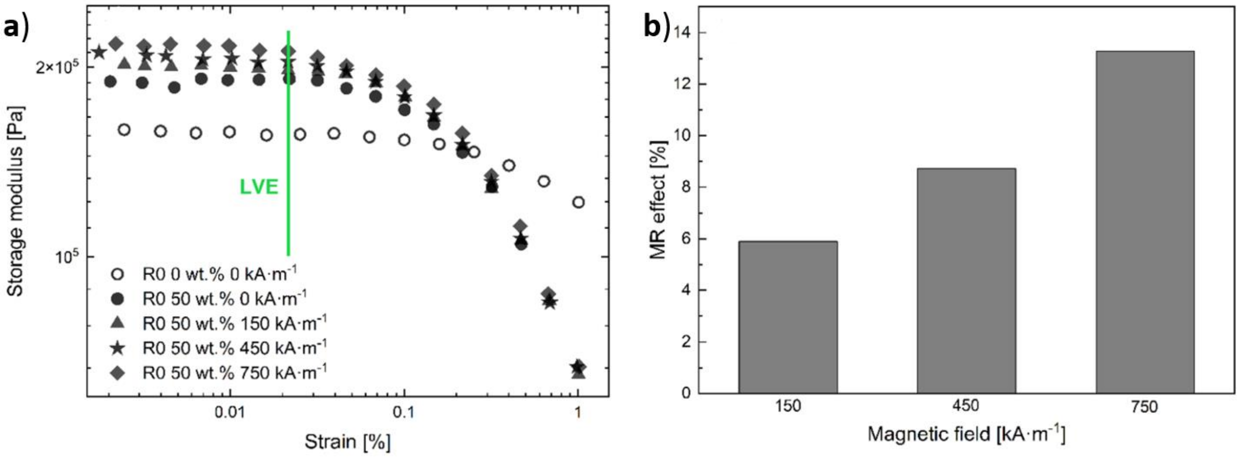

Figure 4.4 a) Dynamic strain sweeps for an MRE containing 50 wt% CI particles at different magnetic fields (filled symbols; circles 0 kA/m; triangles 150 kA/m; stars 450 kA/m; diamonds 750 kA/m); the neat matrix (unfilled) and (b) MR effect for the same 50 wt% matrix [52].

4.5 Particle-matrix interaction within MREs

As mentioned above, highly filled thermoplastic MREs did not display an MR effect while MREs with a less amount of filling did. This unexpected result was explained through the particle-matrix interactions during reprocessing. Dynamic time sweeps were performed to simulate the samples during reprocessing and they are shown in **Fig. 4.9**. For these measurements, the temperature was set to the processing one at 180 °C, and the sample was quickly loaded trimmed and measured. For the neat elastomer in **Fig. 4.9a**, a typical curve is extracted with the *G'* decreasing over time as the sample is heated and softens. The 30 wt% MRE shows the same decreasing trend for the first hour however, right after the *G'* is increased. The same elastomer is shown in **Fig. 4.9b** at a different scale together with the MRE with 80 wt% which shows a *G'* that is increasing for more than an order of magnitude. This increasement of *G'* has to do with the particle-matrix interactions. The thermoplastic elastomer is composed of polyurethane groups which can easily produce free radicals at the processing temperatures. Additionally, the CI particles are covered with a hydroxyl layer which can also produce radicals. Thus, a meeting of these radicals will result in a covalent bond which is demonstrated by the stiffening of the material. For the 30 wt% MRE, there are few particles and the softening due heating has a higher impact on the *G'*. However, after an hour the bonding process becomes dominant. For the 80 wt% particles on the other hand, the bonding formation is instantaneous and the amount of bonds is high enough to overcome the softening by a large amount. This explains why only the unprocessed sample displayed an MR effect. During the recycling processes the magnetic particles bond with the matrix and thus are not able to move and form any kind of structures.

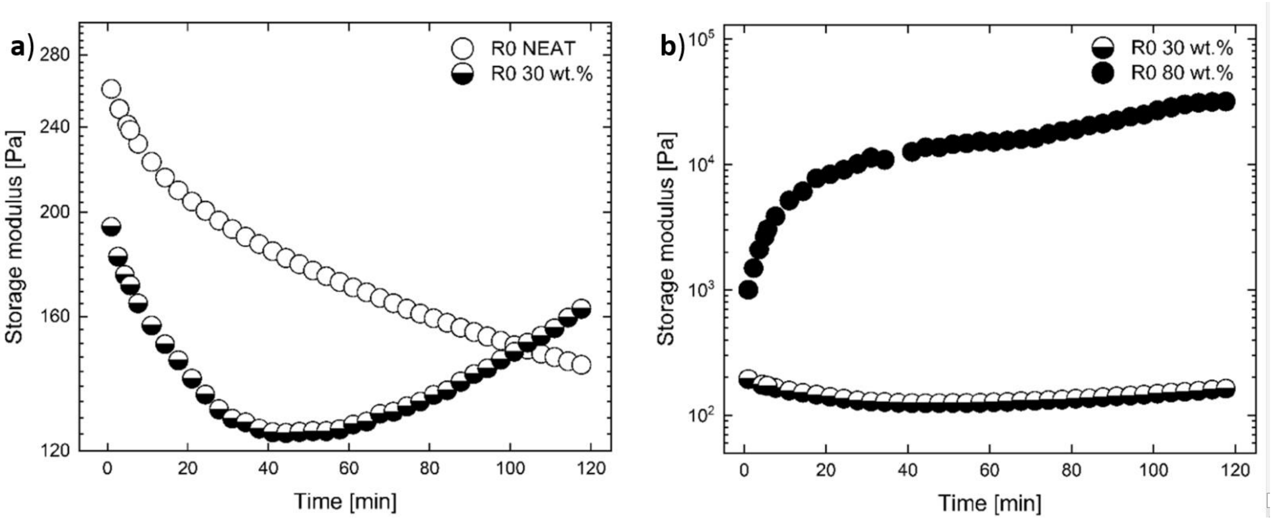

Figure 4.5 Dynamic time sweeps for (a) unprocessed pure elastomer (open circles) and the 30 wt% MRE (half open circles) and (b) 30 wt% MRE and the 80 wt% (filled circles) [52].

5. CONCLUDING REMARKS

5.1 Evaluation and summary of the Ph.D. goals

There were five general goals in total set for this Ph.D. study. The goals had to do with the marriage between the fundamental research of the MR systems with their applications. Each goal is evaluated separably as follows:

- Studies of various polypyrrole-based MRFs were conducted. In particular, the previous PPy nanotube synthesis methods are now optimized. Two types of PPy composites were prepared. The former include magnetite nanoparticles decorated on the PPy nanotubes in various concentrations. The amount of the magnetite nanoparticles can be easily manipulated through the solutes of the rection. The latter includes nickel microparticles coated with PPy nanoparticles. Both types of composites were extensively studied in MRFs.

- An investigation of the impact of the abovementioned magnetic nanotubes in conventional MRFs was conducted. Various types of the abovementioned PPy nanotubes (with higher or lower amounts of magnetite nanoparticles) were mixed in small amounts with a conventional CI-based MRF. The resulting MRF showed superior MR properties with a greater sedimentation stability.

- Several electrical devices composed of MRFs were prepared. The MRFs were composed of both the PPy nanotubes decorated with magnetite and nickel particles coated with PPy particles of different morphology. The electrical devices took advantage of the dual conductive and magnetic nature of these types of particles. The devices could be used both as a mean to characterize MRFs and as devices with tunable electrical properties.

- Recyclable MREs were prepared based on a thermoplastic polyurethane and CI particles. The mechanical properties were compared to the pure analogue elastomer and its recycled pallets. It was concluded that for an 100% recycled MRE, the material properties are not supressed significantly. Additionally, some of the other properties, such as the piezoresistivity, were preserved even after three reprocessing cycles however, the MR behaviour was only observed for some of the samples and only for a single reprocessing cycle due to the development of a covalent bonding between the particles and the matrix.

- During processing of MREs or when they are exposed to elevated temperature, the polymeric matrix may react with the surface of the magnetic particles. These interactions were studied for two types of elastomers including a polyurethane-based thermoplastic elastomer with numerous active groups that promote the particle-matrix interactions. The second elastomer was a polypropylene-based thermoplastic elastomer which has no active groups and theoretically, should show no signs of bonding. The particle-matrix interactions were mainly evaluated through rheology and proposed mechanisms were suggested.

- Most of the abovementioned studies are already published in Q1/Q2 impact factor journals, thus it can be said that the goals are generally achieved. The papers counted for this Ph.D. are the following:

  1) Anitas EM, **Munteanu A**, Sedlacik M, Bica I, Munteanu L, Stejskal J. Magnetic and electric effects in magnetorheological suspensions based on silicone oil and polypyrrole nanotubes decorated with magnetite nanoparticles. Results in Physics. 2024;61:107768.**Munteanu A**,
  2) **Munteanu A**, Plachý T, Munteanu L, Ngwabebhoh FA, Stejskal J, Trchová M, et al. Bidisperse magnetorheological fluids utilizing composite polypyrrole nanotubes/magnetite nanoparticles and carbonyl iron microspheres. Rheologica Acta. 2023;62(9):461-72.
  3) **Munteanu A**, Ronzova A, Kutalkova E, Drohsler P, Moucka R, Kracalik M, et al. Reprocessed magnetorheological elastomers with reduced carbon footprint and their piezoresistive properties. Scientific Reports. 2022;12(1):12041.
  4) Jurča M, Vilčáková J, Kazantseva NE, **Munteanu A**, Munteanu L, Sedlačík M, et al. Conducting and magnetic hybrid polypyrrole/nickel composites and their application in magnetorheology. Materials. 2023;17(1):151.

5.2 Summary of the research work reports

A summary of the published papers in regards to the abovementioned goals is given below:

- **Article I** titled “Magnetic and electric effects in magnetorheological suspensions based on silicone oil and polypyrrole nanotubes decorated with magnetite nanoparticles”

Paper overview: Polypyrrole-magnetite composites-based magnetorheological fluids were prepared and used as parts of an electric device with tunable resistivity and capacitance.

Two MRFs composed of two different types of PPy nanotubes decorated with magnetite nanoparticles dispersed in silicone oil were investigated. One type of the nanotubes is more conductive while the second more magnetic. The MRFs were used as dielectric materials as part of an electrical device which operates in external magnetic and electric fields. The resistance and the capacitance of the device are then measured under external fields. The trends of the resistance and capacitates follow the dipolar approximation model. It was found that it is possible to tune the equivalent resistance and the capacitance by changing the values of the external electric and magnetic fields. The system responds better to magnetic fields allowing the capacitance and the resistance to be tuned much easier for the nanotubes with the highest amount of magnetite nanoparticles.

- **Article II** titled "Bidisperse magnetorheological fluids utilizing composite polypyrrole nanotubes/magnetite nanoparticles and carbonyl iron microspheres".

Paper overview: Evaluation of the MR performance and the stability of a dimorphic MRF based on CI microspheres and PPy-magnetite nanotubes.

In this work two types of magnetic PPy nanotubes which were decorated with different amounts of magnetite were synthesized using a new method. The method allows for nanotubes with tunable magnetic and electric properties to be synthesized. These nanotubes were mixed with a conventional CI-based MRF and this is the first study which investigates the combination of spherical and tube-like magnetic particles. The flow behaviour of the DMRFs was compared with a conventional MRF. The two systems showed similar flow-properties however, one of the DMRFs showed a higher stress increased during the on-state, especially at low magnetic fields. This was attributed to the faster magnetic saturation of the nanotubes over the CI-based particles. The experiments were performed also at elevated temperatures where it was proven that both DMRFs have a better MR response. Lastly, the stability of the systems was investigated with both DMRFs showing a greater sedimentation stability over the conventional MRF.

Author contribution: conceptualization, investigation, writing-original draft.

- **Article III** titled "Reprocessed magnetorheological elastomers with reduced carbon footprint and their piezoresistive properties".

Paper overview: A study of the mechanical and piezoresistive properties of thermoplastic MREs based on a polyurethane matrix after several reprocessing cycles and the interactions between the matrix and the magnetic particles.

This research presents a unique type of MRE which is able to be reprocessed several times while keeping the mechanical properties almost at the same level, with just a ~10% reduction. In total three reprocessing cycles were performed with the material being destroyed and then recycled repetitively. The internal structure, MR performance and the piezoresistivity of these MREs and their pure analogues were evaluated. The MR effect was greatly supressed due to the new internal structure of the MRE which contained covalent bonds between the polyurethane matrix and the magnetic particles. The elastomers' molecular weight was reduced which seemed to the cause of the reduction in the mechanical properties. Surprisingly, the Payne effect was not spotted despite the MREs being highly filled. Lastly, the piezoresistivity tests showed a slight drop in the conductivity after each recycling process however, the changes did not significantly affect the final product. The study is significant as usually only one third of the reprocessed material are used however, this study showed a usable final product composed of 100% recycled materials.

Author contribution: conceptualization, investigation, writing-original draft.

- **Article IV** titled "Conducting and magnetic hybrid polypyrrole/nickel composites and their application in magnetorheology"

Paper overview: Synthesis of hybrid organic/inorganic composites with dual electrically conductive and ferromagnetic behaviour and their application in magnetorheology.

Under the presence of ammonium peroxydisulfate, it was possible to coat nickel microparticles with PPy in a globular and tube-like morphology. The conductivity of composites was in the order of 10^{-1} S cm^{-1} while the magnetic properties depended heavily on the content of nickel. The morphology of the coating played a small role in the conducting and magnetic properties of these particles. The globular composites with two different amounts of nickel were dispersed in a silicone oil and the magnetorheological properties of the system were then evaluated. Depending on the amount of nickel, the MR effect was found between 7–15 which was higher than other nickel-based MRFs from the literature.

Author contribution: investigation, writing, reviewing, and editing.

5.3 Contribution to science

There were several contributions to science through the papers published in this thesis. To be precise:

- An established synthesis method to prepare PPy nanotubes was used. However, several modifications were included which led to the diminish of the residual particles (not tubes) in the system after the synthesis and greatly improved the effective yield of PPy nanotubes.

- For the first time, a DMRF composed of magnetic particles with tube and spherical morphologies were studied.

- The effect of particles that start saturating at different fields was evaluated for the first time.

- For the first time, recyclable MREs with piezoresistive properties were prepared and studied.

- For the first time, the interactions between the filler and the matrix were investigated for MREs under processing conditions. Before these were only speculated. These findings can be easily implemented for any polymer composites.

- The "library of science" was enriched with various MRFs and MREs being included in terms of their mechanical, electrical and magnetic properties.

5.4 Future work

There are several current projects that are being finalized with the manuscripts being in their final states. These include:

- **Future Article I** titled "Processing-Induced Particle/Matrix Interactions in Magnetorheological Elastomers Based on Thermoplastic Matrix"

In this study, a detail investigation is performed on the interactions between the magnetic particles and a matrix of a thermoplastic MRE. The manuscript is finished and in the processed of being submitting before then end of 2024. A first authorship is expected.

- **Future Article II** titled "Tunable Electrical Conductivity of Nickel-Polypyrrole Microparticles Suspensions under Electric and Magnetic Fields"

This is a finished manuscript very similar with the ones explain in section 4.2 with a nickel-based MRF instead of the MRF 6 and MRF 2.5. Currently it is reviewed from the co-authors from University of Timisoara and it is expected to be submitted before the date of the Ph.D. defence. A co-authorship is expected from this study.

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LIST OF SYMBOLS AND ABBREVIATIONS

CI	Carbonyl Iron
DFS	Dynamic frequency sweep
DMRF	Dimorphic magnetorheological fluid
DSS	Dynamic strain sweep
DTS	Dynamic time sweep
ED	Electric device
LVE	Linear viscoelastic regime
MR	Magnetorheological
MRE	Magnetorheological elastomer
MRF	Magnetorheological fluid
b	Magnetic coupling parameter
e_r	Magnetorheological effect
G	Gravitational acceleration
G'	Storage modulus
G'_{off}	G' during the off-state
G'_{on}	G' during the on-state
G''	Loss Modulus
G^*	Complex modulus
H	Magnetic field
k_B	Boltzmann's constant
m	Magnetization of a dipole
M_m	Magnetization of the suspension
Mn	Mason number
Ms	Saturation magnetization
Mw	Polymer molecular weight
n_m	Viscosity of the continuous phase
Pe	Peclet number
PPy	Polypyrrole
R	Radius of a spherical particle
r	Distance between magnetic moments
T	Absolute temperature
T_g	Glass transition temperature
U	Dipole potential energy
u_s	Sedimentation velocity
$\dot{\gamma}$	Shear rate
γ_L	Critical strain
δ	Phase angle
η_{off}	Shear viscosity during the off-state
η_{on}	Shear viscosity during the on-state
Θ	Angle between magnetic moments
λ	Lamda parameter
μ_0	Permeability of free space
μ_m	Permeability of the continuous phase
V	Kinematic viscosity
ρ_p	Density of particles

ρ_s	Density of solvent
T	Shear stress
τ_{off}	Shear stress during the off-state
τ_{on}	Shear stress during the on-state
τ_y	Yield stress

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2021 **Member**	Grant TBU IGA/CPS/2021/003 Piezorezistivity of Advanced Materials
2022 **Principle investigator**	Grant TBU IGA/CPS/2022/004 Magneto-responsive Systems
2023 **Member**	MŠMT DKRVO RP/CPS/2022/007 Smart nanomaterials: from basics to application
2023	Grant TBU IGA/CPS/2023/004

Member	Stability of Magnetorheological Elastomers
2023-present	Czech Science Foundation 23-07244S
Member	Anisotropic Magnetorheological Elastomers with Controlled Electrical Properties
2024	MEYS INTER-EXCELLENCE II LUABA24039
Member	Development of magnetoactive elastomeric Surfaces with controlled wettability for functional Liquid Manipulation - SALMON

Conferences

2022	European Polymer Progress, Prague
Poster	Recycled Polymer Composites with Magnetic Properties
2023	International Congress on Rheology, Athens
Poster	Magnetorheology of Dimorphic Fluids: The Case of Nanotubes-Microspheres System

Mobility

April-May 2023	Johannes Kepler University Linz, Austria.

LIST OF PUBLICATIONS

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1. **Munteanu A**, Ronzova A, Kutalkova E, Drohsler P, Moucka R, Kracalik M, et al. Reprocessed magnetorheological elastomers with reduced carbon footprint and their piezoresistive properties. Scientific Reports. 2022;12(1):12041.
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ACCEPTED MANUSCRIPTS

7. **Munteanu A**, Sedlacik M. Progress in Surface Functionalized Particle-based Magnetorheological Composites. 2023.
8. Anitas EM, **Munteanu A**, Sedlacik M, Bica I, Munteanu L, Stejskal J. Magnetic and electric effects in magnetorheological suspensions based on silicone oil and polypyrrole nanotubes decorated with magnetite nanoparticles. Results in Physics. 2024;61:107768.

SUBMITTED MANUSCRIPTS

9. Munteanu L, **Munteanu A**, Sedlacik M. Electrorheology a material open review. Progress in material science 2024

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Viscoelastic Response of Magnetorheological Suspensions

Viskoelastická odezva magnetoreologických suspenzí

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