Novel shear thickening and magnetorheological materials and their application in controllable electrolytes

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Novel Shear Thickening and Magnetorheological Materials and Their Application in Controllable Electrolytes

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2016
Abstract

Shear viscosity is used as a parameter that characterizes the energy dissipation rate under shear loading. For instance, shear viscosity for Newtonian fluid is an intrinsic material parameter and independent of shear rate. Through the method of suspending small particles inside of the Newtonian fluid, particle concentration is formed and exhibits a number of rheological phenomena, for instance, shear thinning, shear thickening, thixotropy, yielding, and shear induced aggregation.

In some occasions, the energy dissipation rate decreases with the increasing shear rate, which means decreased shear viscosity and corresponding shear stress increases below linearity with the respect to shear rate, it is defined as shear thinning.

To the other end of the spectrum, another type of non-Newtonian behavior, in which a steep rise in shear viscosity is observed and corresponding shear stress increases faster than linearity with respect to shear rate, it is defined as Shear Thickening (ST).

Although this counter intuitive phenomenon of ST was initially viewed as a problem, for instance, complicating and limiting the rate of industrial processes which involved combination of high shear rates and highly concentrated suspensions such as paper coating and pumping of slurries, the unique material properties, such as increased energy dissipation together with increased elastic modulus, make the shear thickening materials very favorable candidates for damping and shock absorption applications. Consequently, engineers and colloid scientists have endeavored to study the science and practical problems of the shear thickening materials. More recently, it is widely proposed that when engineered into composite materials, Shear Thickening Fluids (STFs) can be controlled and harnessed, and thus triggers the development of large number of novel fluids or elastomer materials featuring shear thickening, which in turn broaden the horizon of shear thickening study, and the application of the shear thickening phenomenon is greatly widened as a result.

Magnetorheology (MR) is a concept referred to as magnetic sensitive particles initiated reversible wide range change in mechanical properties and even phase
alternation through the formation of chain like alignments under external magnetic field. It has been intensively studied and widely applied in modern mechanical products and civil infrastructures, as it bears huge potential as a simple, quiet, and rapid-response interface between electronic control and mechanical systems.

In this thesis, we propose a novel magnetorheological shear thickening fluid (MRSTF), which exhibits dual function of both magnetic controllable mechanical properties as well as shear thickening behavior in a unified system. As revealed by the systematic experimental study, including steady shear, oscillatory shear, stress relaxation and strain creep tests, the mechanical properties of MRSTF are investigated; and different working modes of the proposed MRSTF are clearly defined. Besides, the experimental results indicate that effective manipulation of shear thickening behaviour may be realized by adjusting magnetic force precisely, thanks to the adoption of magnetic sensitive components in MRSTF.

Moreover, experiments have also been conducted to study the potential to apply both ST and MR concepts to new generation gelled or solid electrolyte that features controllability, safety, high conductivity and improved impact resistance together with the application of ionic liquids (ILs)

An ionic liquid shear thickening fluid (ILSTF) is presented where obvious shear thickening behavior is achieved on top of the original Newtonian behaviour of the IL medium. An improved conductivity is also observed at certain condition. Thus, it indicates successful adoption of ST phenomenon to novel liquid electrolyte.

A liquid form magnetorheological electrolyte (MR electrolyte) is also developed, where the phase of the material could be reversibly controlled by external magnetic field between liquid and semi-solid without negatively affecting conductivity, which is beneficial in protecting electro-chemical devices adopting such novel electrolyte against mechanical abuse.

Lastly, an elastomeric counterpart of MR electrolyte, namely magnetorheological ionogel (MR ionogel), is presented as a novel solid electrolyte, which eliminates the necessity of in-use magnetic field thus streamlines the complexity of systems that
Abstract

adopt such material. This is due to the fact that MR ionogel exhibits affinity to specific fabrication condition, which allows pre-defined physical properties.

On the whole, this research has contributed towards a better understanding of the mechanism and hybridisation of the concepts of magnetorheology and shear thickening, as well as being a worthy discussion of the application of novel smart materials in electrolyte study.

The list of publication arising from the thesis is as following:

- Tailoring of physical properties of ionogel from magnetic prospective (in preparation)
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List of Symbols

$\tau_y$  Yield stress

$\tau_{yd}$  Dynamic Yield Stress

$\tau_0$  Constant Shear Stress

$\gamma$  Shear Strain

$\gamma_s$  Instantaneous Creep Strain

$\gamma_e$  Elastic Strain

$\gamma_p$  Plastic Strain

$\gamma_d$  Retardation Strain

$\gamma_v$  Viscous Strain

$\gamma_C$  Creep Strain

$\gamma_k$  Recovery Strain

$\gamma_0$  Strain Amplitude

$\gamma_{lin}$  Critical Strain

$\dot{\gamma}$  Shear Strain Rate

$J_C$  Creep Modulus

$J_R$  Recovery Modulus

$\eta$  Shear viscosity

$\eta^*$  Complex Viscosity

$\eta'$  Real Part of Complex Viscosity

$\eta''$  Imaginary Part of Complex Viscosity
### List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>( H )</td>
<td>Magnetic Field Strength</td>
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<tr>
<td>( G' )</td>
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</tr>
<tr>
<td>( G'' )</td>
<td>Loss Shear Modulus</td>
</tr>
<tr>
<td>( \delta )</td>
<td>Loss Angle</td>
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<tr>
<td>( G'_{m} )</td>
<td>m-th storage modulus</td>
</tr>
<tr>
<td>( G''_{m} )</td>
<td>m-th loss modulus</td>
</tr>
<tr>
<td>( B )</td>
<td>Magnetic Flux Density</td>
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<td>( \omega )</td>
<td>Angular Frequency</td>
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<td>( A )</td>
<td>Conductive Area</td>
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<tr>
<td>( R_{c} )</td>
<td>Impedance</td>
</tr>
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<td>( L )</td>
<td>Gap Between Electrodes</td>
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<tr>
<td>( \alpha )</td>
<td>Conductivity</td>
</tr>
<tr>
<td>( h(\gamma) )</td>
<td>Damping Function</td>
</tr>
<tr>
<td>( G(t, \gamma) )</td>
<td>Stress Relaxation Modulus</td>
</tr>
<tr>
<td>( G_{p} )</td>
<td>Plateau of Stress Relaxation Modulus</td>
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Chapter 1 Introduction

1.1 Motivation and Objectives

Recent developments in intelligent materials have taken the direction of designing and applying new engineering materials with highly functional changeable and even integrated properties. The merits of new intelligent materials include offering optimised performance of existing engineering products as well as opting new solutions with improved and/or more robust capabilities. They can be versatility used in practical structures like sensors and actuators [1-3]. Thanks to this, scientists and technicians today are able to realise precise remote control of complicated mechanical structures safely under extreme environments [4-7]. Consequently, the field of intelligent materials research has attracted a large number of researchers and huge financial investments all around the world, a large number of new materials are proposed, designed and applied in every aspect of our lives. Constantly improving existing materials and triggering meaningful inter-disciplinary study are the essential requirement and powerful drive to the modern intelligent materials study.

Featuring active field control and responsive mechanical properties, magnetorheology (MR) and shear thickening (ST) behaviour are separately two important branches in the development of intelligent materials, however, there hasn’t been comprehensive study on the possible combination of these two physical phenomena. Consequently, an important motivation of this research thesis is to propose a novel smart material that is able to operate in shear thickening mode and to exhibit sensitivity to external magnetic field.

Moreover, the current electrolyte research hasn’t been a satisfactory from the prospective of safety and durability, extra care is required due to the active chemistry properties of organic liquid electrolyte. Nevertheless, existing solid electrolytes couldn’t provide equal performance comparing to their liquid counterparts. In light of this, another important objective of this thesis is to introduce MR and ST phenomena
Chapter 1 Introduction

to a unique conductive medium of ionic liquids (ILs), so as to achieve controllable fortifying effects upon mechanical abuse while maintaining and/or improving conductivity of the electrolyte materials.

Some basic information about magnetorheology (MR), shear thickening (ST) and ionic liquids (ILs), which are key components of this research thesis, are listed in following paragraphs.

MR materials are a family of intelligent materials that are able to exhibit reversible and fast response to the presence of external magnetic fields [8,9]. Conventionally, the most common kind of MR materials is magnetorheological fluids (MRFs), which refers to as dispersions of micron-sized highly magnetisable particles in non-magnetic carrier fluids [10]. When the sizes of dispersing magnetisable particles are down to nano-scale, the dispersion is then categorised as ferro-fluids (FFs) [11]. Other kinds of MR composites also exist as solid counterparts of MRFs and ferro-fluids, they are, namely, magnetorheological gels (MRGs) and magnetorheological elastomers (MREs) [12-14]. Beside these MR materials, other types of MR related materials are also employed occasionally, for instance, magnetorheological plastomers (MRPs) and inverse ferro-fluids (IFFs) [15,16]. The large family of MR materials have vastly power human’s ability to maneuver mechanical systems, and they are competitive candidates to a lot more revolutionary inventions.

The phenomenon of ST refers to the ability of colloidal dispersions to harden upon rapid external shear loading. Due to the fact that shear thickening fluids (STFs) can provide simple, quiet, passive yet rapid response to dramatic external shearing deformation, the most attractive application of STFs is serving as an improvement to current human protection facilities with a large number of patents granted [17-19].

Ionic liquids are molten salts, composed entirely of ions, and the melting temperatures are usually below 100 °C [20]. They may act as catalysts for chemical reactions, solvents for bioscience studies, or next generation of electrolytes for batteries and fuel cells [21], due to some of the properties, like, non-flammability, negligible vapor pressure, thermal stability, chemical stability, and high ionic conductivity [22-25].

To summarise, the most important motivation and exciting objective of this thesis is to
explore an applicable path that could cross-link the advantages of well-developed physical phenomena of MR and ST. Thus, this thesis proposes novel intelligent materials as satisfactory solution or improvement to existing technological concerns.

1.2 Scope

This thesis composes of three sections: (1) experimental and modeling study of magnetorheological shear thickening fluid (MRSTF) under varied flow modes, so as to understand the combining effect of magnetorheology and shear thickening phenomenon; (2) application of the concepts of ST and MR to liquid electrolyte; (3) fabrication and experimental evaluation of magnetorheological ionogel (MR ionogel).

In the first section, experiments will be conducted to obtain the rheological responses of MRSTF under steady shear, oscillatory shear, relaxation and creep experiments with an advanced stress controlled rheometer with plate-plate configuration. Various loading conditions and environment factors are considered to reveal an entire picture of the material. Multi-parameter mechanical models are also applied to scale the complex behaviour of the MRSTF under varied experimental conditions. The macroscopic phenomena obtained from the experimental study are substantially explained and linked to microstructural mechanism of MRSTF.

The second section of this thesis explores both passive (shear thickening) and active (magnetorheological) construction of internal microstructures in new generation of liquid electrolyte, where an ionic liquid shear thickening fluid (ILSTF) and a magnetorheological electrolyte (MR electrolyte) are proposed. Experiments are carried out with varied mechanical, electro-chemical and microscopic facilities, so as to justify the effectiveness of the proposed electrolytes.

The third section of this thesis, as an extension of the second part, explores the permanent establishment of controllable magnetorheological microstructures in a solid platform of UV initiated ionogel. Experiments are carried out to this MR ionogel fabricated under different conditions with electro-chemical, mechanical and microscopic facilities, so as to understand how external magnetic field could affect
the physical properties of the proposed MR ionogel.

The frame of the thesis content is briefly summarised in the following table.

<table>
<thead>
<tr>
<th>Physical Phenomena</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Magnetorheology</strong></td>
<td><strong>Shear Thickening</strong></td>
</tr>
<tr>
<td><strong>Magnetorheological Shear Thickening Fluid</strong></td>
<td>A novel presentation of both magnetorheological effect and shear thickening effect in a unified system demonstrating clear working modes according to external shear loading and magnetic field</td>
</tr>
<tr>
<td><strong>Magnetorheological Electrolyte</strong></td>
<td><strong>Ionic Liquid Shear Thickening Fluid</strong></td>
</tr>
<tr>
<td>A novel actively switchable liquid electrolyte based on low-viscosity high performance ionic liquid that maintains conductivity despite alternation of physical appearance upon external magnetic field</td>
<td>A novel anti-impact liquid electrolyte based on ionic liquid that exhibits both satisfactory conductivity and pronounced shear thickening behavior upon external shear loading</td>
</tr>
<tr>
<td><strong>Magnetorheological Ionogel</strong></td>
<td></td>
</tr>
<tr>
<td>A novel elastomeric solid electrolyte fabricated through convenient UV initiating method that possesses structured iron alignment and high conductive content of ionic liquids, thus exhibits sound mechanical strength, and at the same time satisfactory conductivity.</td>
<td></td>
</tr>
</tbody>
</table>

1.3 Organization of the thesis

Chapter 1 provides an introduction to the nature, motivation and scope of this research.

Chapter 2 outlines the important technological issues concerning and a list of milestone researches on the context of magnetorheology, shear thickening and ionic
liquids, which are key components in the current research.

The first section of this thesis is then reported from Chapter 3 to 5. In Chapter 3, an extensive study of both dynamic and steady shear rheology of MRSTF under various environment conditions is presented. Modelling approach is applied to summarise the complex behavior of MRSTF. Then the MRSTF is experimentally defined through stress relaxation experiment in Chapter 4 and the instantaneous flow behavior of MRSTF is explained in strain creep and recovery experiment in Chapter 5.

The second section of this thesis presents the introduction of shear thickening phenomenon and magnetorheology to ionic liquid based liquid electrolyte in Chapter 6 and 7, respectively.

The third section of this thesis is given in Chapter 8, which explains the fabrication and physical properties of MR ionogel with a brief discussion of the structural manipulation through magnetic fields applied at different intensities.

Chapter 9 summarises the main findings of this research and proposes future work.
Chapter 2 Literature Review

2.1 Introduction

Intelligent materials, or smart materials, are materials with highly functional and changeable properties, and have been attractive in recent development of science and technology. The beauty of intelligent materials is that they could assume practical structures upon variation of environmental factors, for instance, temperature, magnetic field, electrical field, pH value and so on. These structural evolutions would lead to macroscopic variations of the materials, such as shape, stiffness, damping, position, fluid flow rate and other characteristics, and have been a constant source to create new products with improved and/or more robust capabilities. Consequently, the number of new generations of sensors and actuators embedded with new smart materials has been vast and updating quickly. Thanks to the endeavor in the past a few decades, there exists big family of intelligent materials used in modern smart structural applications, including magnetorheological materials, shear thickening materials, electro-rheological materials, piezoelectric ceramics, shape memory alloys and so on [1-5].

The MR materials and STFs are both important branches in the research of intelligent materials. Thus, in this chapter, we will define both phenomena and review the context of research regarding both classes of intelligent materials, as well as the already wide spread applications of both kinds of materials.

Besides, the study of both liquid and/or solid electrolytes involving ionic liquids (ILs) will also be substantially reviewed, as an important topic in this research is to transfer the structural controllability to ILs based novel electrolyte.
2.2 Magnetorheological (MR) Materials

2.2.1 Introduction

Magnetorheological (MR) materials are a class of intelligent materials that possess the ability to alter mechanical properties in a controlled manner upon the application of external magnetic field. And the most advantageous fact for these magnetorheological materials is that the field induced property is both reversible and fast responsive within several milliseconds. Since the first observation of MR effect by Rabinow [26] on the suspension of micron-sized magnetisable particles in a low shear viscosity non-magnetisable fluid, large variety of MR materials assuming different forms have been developed and applied in various engineering facilities. Thus, in the following subsections, we will identify the knowledge of MR fluids and their non-liquid counterparts [11-16] MR elastomers. The vastly applied engineering prototypes featuring MR materials as well as their characterisation techniques will also be briefly reviewed.

2.2.2 Magnetorheological fluids (MRFs)

2.2.2.1 Composition of MRFs and MR effect

A typical MR fluid involves three components, which are ferromagnetic particles, carrier fluid and stabiliser, respectively.

Ferromagnetic particles

The ideal candidates for the dispersing phase of MRFs are magnetosoft particles with negligible residue magnetisation and can be dispersed randomly in fluids. The size of particles is preferred within the range of 1-10 μm, however, sub-micron and larger particles are also seen. And the shape of dispersing particles is generally spherical. The so-called carbonyl iron particles fabricated through thermal decomposition of iron penta-carbonyl or reduced iron particles are most commonly used satisfying all
the criteria, however, more expensive alloy particles such as iron-cobalt and iron-nickel alloy particles may also be adopted.

*Carrier fluid*

The requirement for the continuous phase of MRFs is low initial shear viscosity, anti-corrosion, low toxicity and reliable temperature stability. Typical choice of carrier fluid includes mineral and silicone oils, polyesters, polyethers, synthetic hydrocarbons and water.

*Stabiliser*

In order to improve the durability and lubricating properties, additional stabiliser may also be involved during fabrication process to ensure MRFs’ agglomerative stability, sediment stability and thermal stability.

![Figure 2.1 A schematic of MR effect in MRFs (a) field off, (b) field on [27]](image)

As it is illustrated in Figure 2.1 [27], the MR effect for MRFs is attributed to the magnetisation of the suspending particles. When external magnetic field is absent (Figure 2.1(a)), particles do not exhibit specific orientation but distribute randomly in carrier fluid, the apparent shear viscosity of the fluid remains low and unchanged. When a magnetic field is applied (Figure 2.1(b)), however, the particles start to be magnetised and attract each other along the direction of the magnetic flux density and form gap spanning anisotropic chain-like structure. Consequently, the field affected fluid would transform to semi-solid state with large dynamic yield stress several orders of magnitudes higher than that at zero field condition, which signals the
minimum requirement to make the suspension to flow. Generally speaking, good MRFs should exhibit sound saturation magnetisation, small coercivity/remanant magnetisation, effective MR effect over wide range of temperature variation, and stability against flocculation and chemical oxidation. Composition, dispersing particle size and volume fraction of the dispersion are considered important factors impacting the field-dependent performance of MRFs. It is also worth to point out that this transformation from liquid state to semi-solid state is nearly instantaneous and reversible.

2.2.2.2 MR formulation

In order to fabricate stable MRFs against possible settling and agglomeration problem, two issues have to be addressed [28]:

a. Severe density different between dispersing phase and continuous phase.

b. Inter-particle interaction that favors aggregation due to large surface area to volume ratios of the micron-sized dispersing particles.

From the particle point of view, reduced size for the dispersing magnetisable particle might provide better stability against sedimentation and abrasiveness. However, a limitation is expected, as the aspect ratio between magnetic force and Brownian force decreases when particle size is approaching nano-scale.

As claimed by Choi et al. [29, 30], grafting low density polymer functional group on top of magnetic particles could provide extra dispersibility, and the change of surface chemistry during this process would help preventing particles coming into close proximity, thus avoids particle oxidation and agglomeration. Despite the fact that these core-shell structured particles would usually exhibit reduced the magnetisation, there also exists specific examples of enhanced MR effects as well as improved dispersing stability through this method [31-34].

Besides, thixotropic agent such as silica nano-particles and other ferro-magnetic colloidal particles, for instance, Co-γ-Fe₂O₃ and CrO₂, could be added to model MRFs as stabilising and thickening agent to prevent sedimentation, due to the steric
repulsion between these additives and the relatively larger dispersing magnetic particles [33, 34].

When all is said about the method of particle engineering and selection of specific stabiliser particles, bi-modal MRFs fabricated by mixing magnetic particles of different sizes is also considered an effective method for stabilizing the dispersions with advantageous outcome of improved MR effect than mono-dispersion of either kind of magnetic particles [35, 36]. The reason of this enhancement in MR effect is explained by the fact that smaller particles tend to move into the gaps between larger particles and to break the aggregates of these larger particles, which lead to increasing anisotropic structures, thus results in larger initial shear viscosity off-field and field-induced stresses than that obtained from mono-dispersed counterparts. See et al. [37] observed similar phenomenon in electro-rheological fluids (ERFs). And particle-level simulation also supported this argument of this enhancement [38].

Alternating carrier fluids may also be considered as an effective method in achieving stable and well performed MRFs. Visco-plastic medium has been proposed to be used to resolve the problem of irreversible sedimentation. Specifically, greases are discovered as a promising candidate carrier fluid due to its inherent yield stress [39]. Thanks to versatile compositions of their ions, the ionic liquids (ILs) have also been studied as carrier fluid of the suspension system [40], and yield growing attention of applying the concept of magnetorheology in conductive applications [41].

Other than the sedimentation stability of MRFs, another important challenge in MRFs fabrication requiring considerable attention is the durability, where the problem is mostly attributed to the oxidation of iron magnetic particles. Carlson [42] describes “in-use-thickening”, which refers to the increase of initial shear viscosity of MRFs over the time. This phenomenon, which is caused by the increase of solid content due to the growth of brittle oxidation surface on top of original magnetic particles, is highly detrimental that causes dramatic decrease in field-induced yield stress due to reduced magnetisation of the particles. Consequently, the loss of durability will eventually turn MRFs into useless paste.
2.2.2.3 Magnetorheology of MRFs

MRFs involved devices demonstrate highly non-linear behavior due to the inherent non-Newtonian behavior of the filler fluid material. Thus accurate models that could predict the field-induced properties of MRFs is a key element in implementing MRFs involved devices. Starting from 1960s, modelling of MRFs (as well as ER counterparts) has received significant attention [38].

Two distinct rheological domains are often mentioned about MRFs operation: the pre-yield and post-yield regions. The pre-yield region possesses a strong visco-elastic nature while the post-yield region exhibits mostly a dominant viscous behavior. These two rheological regimes are separated by a yield point that varies with the application of different magnetic fields. When it comes to describe the flow of MRFs, shear strain rate, temperature, volume fraction and the strength of external magnetic field are considered as important variables.

MRFs show strong field dependent shear modulus and shear stress that resists the flow of the liquid material until a critical point is reached, which is the yield point mentioned in previous paragraph. To describe such characteristic, a Bingham plastic model featuring the classical Newtonian definition of apparent shear viscosity as quotient of shear stress and shear strain rate is often used, as given in Figure 2.2.

Where $\tau_0$ stands for the field dependent yield stress, $\eta$ is the constant plastic viscosity. In this figure of Bingham plastic model assumes MRFs behave like Newtonian fluid in the post-yield region, while possessing constant plastic viscosity [43]. And the following set of equations gives details of the model:

$$\tau = \tau_0 (H) \text{sgn} \dot{\gamma} + \eta \dot{\gamma} \quad |\tau| \geq |\tau_0| \quad 2.1a$$

$$\dot{\gamma} = 0 \quad |\tau| \leq |\tau_0| \quad 2.1b$$
Though this Bingham model has guided the design and development of MR devices in many ways, the assumption that MRFs possess a constant plastic viscosity is not valid. As pointed by Li [44], MRFs show more complex behavior than the linear prediction of Bingham model.

In order to accurately scale the rheological behavior of MRFs, Herschel-Bulkley model is applied by replacing the constant viscosity in Bingham equation into a power index related apparent shear viscosity which takes the form as following:

\[ \dot{\gamma} = 0 \quad |\tau| \leq |\tau_0| \]  \hspace{1cm} 2.2a

\[ \tau = \tau_0 (H) \text{sgn}(\dot{\gamma}) + k |\dot{\gamma}|^{n-1} |\dot{\gamma}| \geq |\tau_0| \]  \hspace{1cm} 2.2b

The apparent shear viscosity is more accurately defined according to Herschel-Bulkley model as given by:

\[ \eta_{app} = k|\dot{\gamma}|^{n-1} \left\{ \begin{array}{ll}
  n < 1 & \text{Shear thinning} \\
  n = 1 & \text{Bingham model} \\
  n > 1 & \text{Shear thickening}
\end{array} \right. \]  \hspace{1cm} 2.3

Equation 2.3 indicates that Herchel-Bulkley provides more complex prediction on the rheological behavior of complex liquid materials, which are shear thinning behavior when \( n<1 \), shear thickening when \( n>1 \), respectively. And the model reduces to Bingham plastic model when \( n=1 \).
2.2.2.4 Physical Mechanisms and Viscoelasticity of MRFs

Till now, there has only been one widely accepted physical mechanism to interpret the field-induced magnetisation and anisotropic interaction of MR materials, which is the so called particle magnetisation model [45]. According to this model, the reason for the formation of the field-induced anisotropic structure is the magnetic permeability difference between the magnetic sensitive magnetic particles and the non-magnetic carrier fluid. Consequently, when external magnetic field is applied to MRFs, this dispersing phase of magnetic particles would experience overwhelming magnetic moment comparing to negligible thermal force (\(\propto kT\)) and behave as magnetic multi-domain. By applying considerable simplification of linear magnetisation that neglects multi-pole and multi-body magnetostatic interactions between the field affected particles and assuming spherical shape of these magnetic particles, an isolated magnetisable particle would acquire a certain magnetic moment as given in Equation 2.4 to be adopted in the anisotropic structure.

\[
m = 4 \pi \mu_0 \mu_r \beta \mu_0^3 H_0
\]

where \(\mu_0 = 4\pi \times 10^7 \text{Tm}^2\) is the permeability of vacuum, \(\mu_r\) is the relative permeability of the continuous phase, \(\beta = (\mu_{pr} - \mu_r)/(\mu_{pr} + 2\mu_r)\) is the contrast factor with \(\mu_{pr}\) being the relative permeability of the particles, and \(H_0\) is the magnetic field strength. At high magnetic field, on the other hand, magnetic particles would reach saturation and couldn’t be further magnetised, then the magnetisation becomes independent of field strength, as given in Equation 2.5

\[
m = \frac{3}{4} \pi \mu_0 \mu_r \beta \mu_0^3 M_s
\]

Another important parameter is \(\lambda\), representing the ratio between the competing elements of magnetostatic force and thermal force, which is considered as a determiner of field-induced structures as given in Equation 2.6:

\[
\lambda = \frac{\pi \mu_0 \mu_r \beta^2 \alpha^3 H_0^2}{2k_B T}
\]
When sufficient external magnetic force is applied, $\lambda$ will take a relatively large value, which favors magnetostatic interactions than thermal force. As a result, dispersing magnetic particles would start to form anisotropic chain-like alignment. When the external field is sufficiently small or the aspect ratio of the dispersing particles is sufficiently small, the thermal force (or Brownian force, if the particles are in nano-scale), which favors isotropic distribution of the particles, will be dominant over the formation of internal structures. As pointed out by Furst and Gast [46], the final equilibrium structure of MRFs is only related to volume fraction $\phi$ and $\lambda$, as mapped in Figure 2.3 [47], where HT stands for Halsey and Toor model [48], which argues that dipolar particles form field-induced chain-like alignment quickly but gradually settle with the relaxation of the chains at relatively dilute dispersion. And MHT stands for modified Halsey and Toor model [49], which argues that the isotropic structure is formed before the chain is relaxed. Besides, Liu et al. [50] also proved through experimental and simulation method that the rate of field increase and container size of MRFs might also cast effect on the final presentation of field-induced structure. The minimum-energy structure might not be multiple chains and columns under fast increasing field intensity, but a labyrinthine pattern that quickly formed instead, depending on the boundary condition, sample concentration and random thermal interactions [51,52].

![Figure 2.3 Dominant mechanisms of lateral interactions of MRFs as a function of](image)
MRFs are a class of viscoelastic liquid, which is often investigated by applying oscillatory flow on them. This is valuable because oscillatory flow is considered a more feasible tool in determining the internal structures of the materials than simple steady shear flow, and practical MR devices are often designed to operate in oscillatory mode.

Parthasarathy and Klingenberg [53] illustrated the frequency and strain dependence of the rheological properties of MRFs in a Pipkin diagram (Figure 2.4). When strain deformation amplitude is small, the liquid system would perform in linear regime of viscoelasticity. With the increase of the strain amplitude, a transition from linear viscoelastic range to non-linear viscoelastic range would be characterised by higher orders of harmonics at a certain strain value ($\gamma_{cr,1}$). As the strain amplitude continues to increase, a transition from non-linear viscoelasticity to viscoplasticity is observed at a second critical value ($\gamma_{cr,2}$). When the strain amplitude and frequency value both reach high values, the elastic properties of MRFs become negligible and the liquid would exhibit Newtonian behaviour.

![Figure 2.4 Pipkin diagram of the dynamic rheological behavior of MR fluids [47, 53].](image)

Small amplitude oscillatory shear (SAOS) test is often used to determine the linear viscoelastic region mentioned in previous paragraph, where the corresponding shear stress of the fluid is in accordance with the applied harmonic strain amplitude. By contrary, when the strain amplitude is above the linear visco-elastic (LVE) range...
determined by the SAOS tests, namely non-linear visco-elastic (NLVE) range, higher order harmonics of the corresponding stress response would start to appear and is no longer in tone with the original strain excitation [54]. Consequently, this transformation from LVE to NLVE range sees significant difference in the dynamic properties of MRFs, and the existing parameters in SAOS are no longer physically meaningful due to the non-linear stress response [55, 56].

Large amplitude oscillatory shear (LAOS) is the most used method to investigate the transition between LVE and NLVE ranges of MRFs [57]. When the strain amplitude is small and within the LVE range, the storage modulus is independent on the strain deformation. However, as the strain amplitude increases beyond the LVE range, an obvious decrease of storage modulus could be observed [58]. Through this method, one could conveniently recognize the transition point between LVE and NLVE range of MRFs.

Another effective method of analysing the transition between LVE and NLVE range is to examine the shape of strain-stress hysteresis loop (Lissajous Curve) [59, 60]. When the actuating strain is within the LVE range, the strain-stress hysteresis loop exhibits elliptical shape, while a non-elliptical curve would appear as the result of higher order harmonics of the corresponding shear stress in case of the NLVE range [61, 62].

2.2.2.5 MRF applications

The most referred to engineering application of MRFs is MR dampers, which have already been used in vehicle suspension, civil buildings and shock absorbers. Generally, MRFs have three different operation modes in actual devices [63], as pointed out in Figure 2.5. The flow mode allows MRFs flow through the orifice between two stationary plates to form a pressure gradient between the two plates. The direct shear mode, which is mostly seen in clutches and brakes, operates when fluid is located between two plates that are moving relatively. As for squeeze mode, the confined MRFs are subjected to perpendicular external load. This squeeze mode is mostly applied in vibration and impact dampers.
Based on flow dynamic theory, the governing equations for these three different modes are listed as following:

**Flow mode**

\[
F_\eta = \frac{12\eta LQ}{\epsilon_0 h^3} A_p \\
F_\tau = \frac{cL_a \tau_0}{h} \text{sgn}(v_0) A_p
\]

where \( \eta \) is fluid viscosity, \( L \) is the effective length of the MR device, \( Q \) is the volumetric flow rate, \( A_p \) is piston area, \( v_0 \) is the motion velocity, \( \omega \) is the average radius of the MR fluid laminar slice, \( h \) is the width of fluid flow, \( c \) is a function of the flow velocity profile with a value range between 2 and 3, \( L_a \) is pole length of the MR device, and \( \tau_0 \) is the yield stress of MR fluid under different external magnetic field.

**Direct shear mode**

\[
F_{sh,\eta} = \frac{\eta \omega L}{h} v_0 \\
F_{sh,\tau} = \omega L_a \tau_0 \text{sgn}(v_0)
\]

All the parameters involved in direct shear mode are the same as those in flow mode.

**Squeeze mode**

\[
F_{sq,\eta} = \frac{3\pi \mu r_p^4}{2(x_0 + x)} v_0 \\
F_{sq,\tau} = \frac{4\pi \tau_0 r_a^3}{3(x_0 + x)} \text{sgn}(v_0)
\]

where \( r_p \) is the radius of the piston, \( r_a \) is the active radius that activates the MRF in
squeeze mode, \( x_0 \) is the initial gap between the bottom of the bobbin and the bottom of the outer cylinder.

The governing equation of MRF device working at different modes could give a precise prediction in the design process. However, in semi-active control strategies for MRF damper involved systems, the hystere tic behavior of MRF damper should be taken into consideration, which takes the following form:

\[
F(t) = f(I, x, \dot{x}, \ddot{x})
\]

where \( F(t) \) is the damping force, \( I \) is the applied current, \( x \), as well as its first and second order of derivatives describes the damper movement. The most used phenomenological model predicting the hysteric behavior of MRF damper is Bouc-Wen model [64].

Featuring advantageous properties such as reversible, fast response, low energy consumption and the performance stability over wide range of temperature, we have seen MRF dampers possess tremendous potential in the development of electronic controlled mechanical systems. Asadi et al. [65] designed a MRF damper based haptic interface for rehabilitation applications, where MR effect is used to simulate real-world resistance for patient to re-gain muscle strength. Han et al. [66] proposed a hybrid mount featuring MRF and a piezo-stack for vibration reduction in dynamic system in a wide frequency range. A large-scale MRF damper is also fabricated by Cheng et al. [67], which is able to provide as much as 500 kN damping. This very device is expected to play an essential role in civil building like high-rise building and bridges.

### 2.2.3 MR elastomers (MREs)

#### 2.2.3.1 Introduction

By changing dispersing matrix, there exists non-liquid counterparts of MRFs, the most mentioned one is MR elastomers (MREs) [14]. Besides, softer matrix based magnetorheological composite materials, for instance, magnetorheological gels
(MRGs) [12,13] and magnetorheological plastomers (MRPs) [15], would accommodate greater range of manipulation of MR effect, thus substantially extend the application of MR materials for specific working conditions.

2.2.3.2 Composition and fabrication MREs

Similar to MRFs, the components of MREs are polarised magnetic particles, elastomer matrix and additives [68-70].

The key requirement for dispersing magnetic particles is their low remnant magnetisation and high saturation magnetisation. The former factor could eliminate the effect of magnetic residual, thus prevent magnetic particles from sticking together after the removal of external magnetic field, while the latter would allow high magnetic permeability of the particles, which leads to less magnetic leakage and stronger inter-particle magnetostatic force, thus maximise the MR effect. The particle size applied in MREs fabrication ranges from a few micro-meters to hundreds of micro-meters [71].

Natural rubber or silicone rubber are considered as most used matrix materials for MREs, as effective barrier to eliminate particle aggregation as well as to improve the compatibility of polymeric matrix that is occasionally applied. These cross-linked network materials allow the dispersion of polarised magnetic particles and served as three-dimensional filler material formed adjacent to the structured dispersing magnetic particles, thus provide necessary support to the density difference between the dispersing magnetic particles and the elastomeric matrices [72].

Silicone oil is usually used as additive to MREs, as the molecules of silicone oil could at one hand enter the gap of matrix materials and lead to increased plasticity and fluidity of MREs, and on the other hand help stabilise the internal stress in the materials that improves the stability of MREs [73].

According to the fabrication process, MREs are divided into two different groups, which are isotropic MREs and anisotropic MREs. At the beginning, all the relevant components of MREs are mixed together thoroughly into a homogenous state, and the
Air bubbles inside of the paste are eliminated usually with vacuum environment. At this stage, magnetic particles still possess some freedom to move around, and pendant curing process. If the resultant uniform materials are cured directly without application of external magnetic field, dispersing particles will maintain the random distribution while the matrix materials are solidifying, which is isotropic MREs. If external magnetic field is applied, the polarised magnetic particles will form chain-like structures along the direction of external magnetic field, this alignment is thus locked permanently with the solidification of matrix materials, which is anisotropic MREs [74]. Depending on the properties of matrix materials, the curing process may be staged at room temperature or elevated temperature [75]. In order to fabricate anisotropic MREs, large magnetic field over 0.8T is usually applied for the establishment of iron particle structures [76]. And the volume fraction of both types of MREs could be large and over 30% vol [14, 77]. The detailed fabrication process is presented in Figure 2.6 [74], the typical SEM figures of separately isotropic MREs and anisotropic MREs are given in Figure 2.7 [78].

Unlike MRFs, whose MR effect stem from structure variation, the MR effect of structure pre-defined MREs originates from the magnetostatic force between magnetic particles. With increase of external magnetic field, the bonding between the magnetic particles will grow and require extra energy to twist and deform the pre-structured MREs, thus lead to greater field-induced yield stress and modulus [79]. Due to the directional alignment of magnetic particles of anisotropic MREs, they possess more significant MR effect than the isotropic MREs, which allows broader application in industry for anisotropic MREs than their isotropic counterparts [80, 81].
2.2.3.3 Properties of MREs

The steady-state properties of MREs are usually evaluated and demonstrated by shear stress-strain curve of the MREs samples. Figure 2.8 [78] gives a typical shear stress-strain curve of example MRE sample at seven different magnetic field intensity from 0 mT to 750 mT with step increase of 125 mT. From this figure, it is found out that the observed MRE sample exhibits obvious MR effect, as the responding shear stress increases dramatically with field strength increase. Besides, the pre-yield region, which is defined as the strain range where strain and stress possesses a linear relation, is around 10%. This range is considerably larger than MRFs, which means MREs operate in mostly pre-yield region.
The visco-elastic properties of MREs could be also examined by dynamic oscillatory test, where harmonic shear loading is applied to MREs sample with different strain amplitude and excitation angular frequency. In this case, the shear strain-stress relationship could be presented in elliptical hysteresis loop. As pointed out by Zhou et al. [78] that the areas of shear strain-stress loop as well as the main axis of the elliptic shape would increase with the increase of external magnetic field, which means that both stiffness and damping properties of MREs vary with external field intensity. This feature is totally different to MRFs, which exhibit only controllable damping capacity. Besides, the stiffness of MREs system is also directly related to loading angular frequency, though the change is relatively small and steady.

### 2.2.3.4 Working principle of MR elastomer devices

For MRFs, where dispersing magnetic particles move freely in carrier fluid and form alignments when subjected to the direction of external magnetic field instantaneously, the direction of alignments is always the same with the external magnetic field. However, considering the magnetic particles structures are pre-defined for MREs, the alignment of MREs are no longer in accordance with external magnetic field. Therefore, the working modes for MREs devices are quite different from those of MRFs devices. Generally speaking, as given in Figure 2.9(a) and (b), MREs usually work in shear mode and squeeze/elongation mode. Besides, due to the soft elastic nature of matrix
material, MREs may also operate in the so-called field-active mode, where MREs deform along the direction of external magnetic field and stage the phenomenon of magnetostriction (Figure 2.9 (c)). The shear and squeeze mode are widely adopted in the design and fabrication of vibration absorber, vibration isolator, engineering mount and compressive spring elements [80-83]. The field-active mode, on the other hand may be used in actuator design.

![Figure 2.9 Operation modes of MREs devices (a) shear mode, (b) squeeze/elongation mode and (c) field-active mode [70]](image)

The most important application of MREs is vibration shock absorber, the material may provide variable stiffness in either shear mode or squeeze mode, so as to change the natural frequency of the entire protected system, thus realize protection function in case of disastrous situation.

For MREs operating in shear mode:

The natural frequency of the MRE shock absorber may be expressed as

$$ f_c = \frac{1}{2\pi} \sqrt{\frac{(G_0 + \Delta G)A}{mh}} $$

where $G_0$ is the initial shear modulus of MRE and $\Delta G$ is the field-induced modulus variation, which is calculated by [84]:

$$ \Delta G = 36\rho\mu_0\mu_1\beta^2\bar{H}_0^2\left(\frac{a}{r_a}\right)^3\zeta $$

where $\beta = (\mu_p - \mu_i)/(\mu_p + 2\mu_i)$, which is roughly 1 with $\mu_i$ being the relative permeability of matrix network, while $\mu_p$ and $\mu_0$ are relative permeability of the magnetic particles and vacuum, respectively. $m$ stands for the mass of the oscillator; $h$
is the thickness of MRE involved in shearing.

For MREs operating in squeeze mode:

Similar form is achieved

\[ f_c = \frac{1}{2\pi} \sqrt{\frac{(E_0 + \Delta E)A}{m\eta}} \]  

where \( E_0 \) is the initial compression modulus of MRE and \( \Delta E \) is the field-induced compression modulus variation, which is calculated by [84]

\[ \Delta E = \frac{\delta}{\zeta} \]  

\[ \delta = C \left\{ 3(1+\zeta)^4[1 - B(1+\zeta)^{-3}] - 2(1+\zeta)^{-3} [1 - B(1+\zeta)^{-3}] \times [3B(1+\zeta)^{-4}] \right\} \]  

\[ C = \frac{3\varphi\zeta}{8\pi^2a^3\mu_0\mu_1} r_a^{-3} \left( \frac{4}{3} \pi a^3 \mu_0\mu_1 \chi \tilde{H}_0 \right)^2 \]  

\[ B = \frac{4}{3} \chi \zeta a^3 r_a^{-3} \]  

where \( \chi \) is the specific susceptibility of dispersing magnetic particle, \( a \) is the radius of the particle, \( \tilde{H}_0 \) is the external magnetic field, \( \zeta = \sum_{j>1} 1/j^3 \approx 1.202 \), \( \zeta \) is the compressive strain, \( \varphi \) is the volume fraction \( r_a \) is the initial distance between two adjacent particles.

2.2.4 Conclusion

In this subsection, a brief review of MR technology is presented concerning the basic material, fabrication method, modelling approach as well as their wide spread applications in industry of MRFs and MREs. It should serve as a valuable preparation of knowledge for the development of new MR related materials.
2.3 Shear Thickening Fluids (STFs)

2.3.1 Shear thickening effect

The rate of energy dissipation during shear flow is determined by viscosity of fluids, which is defined as the ratio of shear stress and shear strain rate. In the case of Newtonian fluids, linear relationship of shear stress and shear strain rate is generally observed, indicating constant viscosity upon variation of shear strain rate. However, non-Newtonian behavior is often exhibited by complex fluid systems, where shear viscosity becomes relevant to the amplitude of shear strain rate. In most cases, the rate of energy dissipation decreases with the increase of shear strain rate, which is referred to as shear thinning. While the opposite trend of ascending rate energy dissipation upon increasing shear rate is also recorded, which is called shear thickening.

Despite to the fact that the phenomenon of shear thickening is counter-intuitive to most observers and less commonly referred to than its counterpart, shear thinning, it actually widely exists. Perhaps, the best known example of shear thickening fluid is densely aqueous cornstarch suspension, which takes the form of liquid during distilled state, but dramatically hardened and becomes solid when sheared or stressed. The change of status is so great that it could even allow a person to step on the surface of a pool that is filled with such liquid, as indicated in Figure 2.10 [18]. When the loading is removed, the shear thickening effect is completely reversed, the shear thickening fluid resumes the ability to flow.

![Figure 2.10 Example of shear thickening fluid made by everyday ingredients [18]](image)
Although shear thickening effect was initially viewed as a serious problem in industry processing that requires densely concentration and large shear rates such as paper coating and pumping of slurries, due to the considerable growth of flow resistance [85,86]. The favorable property of effective energy dissipation has opened up opportunities to apply shear thickening fluids as intelligent materials that are responsive to dramatic shear loading [87-90].

2.3.2 Composition and fabrication of STFs

Particle based STFs

A typical STF is composed of carrier fluid and rigid Brownian colloidal particles ranging between 1 nm to 1 \( \mu \) m. Thanks to the wide application and availability as well as well-defined surface chemistry, fume silica nano-particles are most commonly seen in shear thickening study [91, 92]. Rather than the fumed silica particles, other types of colloidal particles are also applied, for instance, Egres \textit{et al.} [93] investigated shear thickening transition of calcium carbonate dispersion through advanced Rheo-SANS technique, as well as titanium oxide and Zirconium dioxide [94, 95]. Besides, synthetically and naturally occurring minerals, polymer beads, and their mixtures are also selected [18, 96-98].

As for the carrier fluid, there has also seen many options including water, ethylene glycol (EG) and polyethylene glycol (PEG). EG or PEG are the most widely used due to their combination of stability, high boiling point, polarity and non-flammable properties [99]. The preparation of most STFs is straightforward by using a low speed mixer.

Beside standing alone STF, shear thickening composites are also proposed by mixing STFs with rubber precursors together with catalyzing agents [100]. As stated by Wagner \textit{et al.} [101], foamed shear thickening composite would exhibit significant shear thickening response by adding STFs to open cell polyurethane. These polymer-blended shear-thickening composites showed unique and superior performance, which was solid like response and absorbing energy at high strain rates.
Chapter 2 Literature Review

while maintaining a liquid like response during low strain rates, due to the involvement of STFs and multiphase microstructures [100]. Another novel shear thickening composite was reported by Caritey et al. [102], which was fabricated by mixing an amphiphilic polymer, hydrophilic particles and PEG together.

**Non-particles based shear thickening materials**

Beside the above mentioned particle based shear thickening systems, there are a few shear thickening systems that exhibit stiffened state at increased shear rate due to segmental mobility of polymers at their glass transition and physically cross-linked polymer networks [103]. Poly(vinyl alcohol) containing boric acid, and, poly(dimethylsiloxane) containing boric acid (key ingredients in Silly Putty™) are two well-known examples of physically cross-linked polymer networks that shear thickened [104].

### 2.3.3 Rheological properties of STFs

Shear thickening is categorised as non-Newtonian behaviour, where effective viscosity increase could be observed with increasing shear rate. There are two important pre-requisites for the expression of shear thickening behavior for complex fluids with colloidal solid particles. The first issue is that the initial status for the dispersing solid particles should be non-aggregating [92], where particles may be stabilised by repulsive pressures from sources including electrostatic forces, steric hindrance and solvation forces without showing net attractive force between particles.

Secondly, shear thickening phenomenon generally could not occur in dilute colloidal particle dispersions. It would only start to show from intermediate particle fractions, since there would be limited particle-particle interaction, thus negligible micro-structural changes, if the particle dispersion is not concentrated [105, 106].

Due to Brownian motion and repulsive stabilisation force experienced by the dispersing colloidal solid particles, STFs mostly exhibit a Newtonian regime at low shear rates, and followed by a shear thinning regime [18], until specific mechanism produces shear stress that starts to grow faster than shear rate at a relatively higher
critical shear rate.

When the particles’ concentration of STFs is at moderate level, the viscosity increase may be relatively mild and continuous at the rate several tens of per cent over a few decades of shear rate increase, thus usually referred to as continuous shear thickening (CST). As the most commonly mentioned shear thickening behavior, continuous shear thickening is substantially studied and modelled in large number of liquid systems. Galindo-Rosales et al. [107] derived a numeric model from fumed silica based shear thickening system, which gives a guideline in predicting a class of STFs and proves the Newtonian and/or Quasi-Newtonian regime before the occurring of shear thickening. Tian et al. [17,108] continued this work by involving temperature as another factor affecting this non-Newtonian behavior of shear thickening. Jiang et al. [109] studied shear thickening behavior of Polymethylmethacrylate (PMMA) polymer beads dispersion in glycerine-water mixture of several fractions. Beside steady shearing technique applied by the above mentioned researches, there were studies concerning dynamic performance of STFs, too. Laun et al. [96] reported the critical strain amplitude for dynamic shear thickening at fixed angular frequency. A fumed silica based STF was investigated by Raghavan et al. [110] through both steady and oscillatory shear tests. Fisher et al. [111] investigated the dynamic response of vibrating sandwiched beam structure based on STFs. These dynamic studies on STFs have come to a conclusion that shear thickening could be observed with a sharp increase of complex viscosity at the critical point that affected by jointly the strain amplitude and angular frequency.

If the particles’ fraction in STFs continues to increase, the degree of viscosity increase tends to increase as well, until a point where the shear induced viscosity or shear stress would jump discontinuously several magnitudes higher at certain critical shear rates. This phenomenon is also widely observed and studied, and referred to as discontinuous shear thickening (DST) [112-114], where effective transition from liquid to solid may be staged and the sheared materials may even crack like a solid [95].

The DST possesses unique rheological properties. For one thing, it can be clearly
defined by a range of shear stress. The onset of dramatic viscosity increase could be characterised by the same critical shear stress, denoted as $\tau_{\text{min}}$, independent of packing fraction. Another critical stress $\tau_{\text{max}}$ that is independent of packing fraction could also be observed, which defines the upper limit of shear induced viscosity increase, and shear thinning and cracking are generally staged when applied stress is beyond the critical value [114, 115].

Both continuous and discontinuous shear thickening are reversible processes, where materials would resume their original liquid state after the removal of external shear loading, and exhibit similar stress or shear viscosity curves at repeating courses of shear rate increase and decrease.

### 2.3.4 Factors affecting shear thickening

There are several factors affecting the onset of shear thickening phenomenon, of which the most important ones are particle concentration, particle size, particle shape, particle size distribution and particle interactions. In this subsection of literature review, all these factors will be addressed one by one:

To start with, the volume fraction of shear thickening dispersion plays a crucial role over the non-linear rheological behavior [116, 117]. When the particle fraction of the dispersions is under a dilute condition, the inter-particle interaction tends to be insignificant, as the flow field of one particle will not influence other surrounding particles. However, as the particle fraction increases, there would exist increasing likelihood of hydrodynamic influence between particles. Thus, the higher of the volume fraction, the greater hydrodynamic force would be, which causes more significant effect on the flow properties of the dispersions [116-118]. Consequently, viscosity of the fluid suspension is more sensitive to shear rate and/or shear stress as particles are strayed away from original equilibrium positions. When the volume fraction of the STFs is extremely large, there would incur greater possibility of discontinuous shear thickening, this dramatic form of shear thickening is due to
combined effect of hydrodynamic force and other mechanisms triggered by concentrated status.

By reviewing the past landmark observation of shear thickening, the relevance of particle fraction is substantially proved regardless the different nature of varied dispersing particles.

In the study of titanium dioxide dispersions in different dispersing medium, Metzner and Whitlock [119] found out stronger shear thickening response of more concentrated test samples, as given in Figure 2.11. As also evidenced by Hoffman [117], the more concentrated PVC latex exhibited greater magnitude of shear induced thickening phenomenon, as illustrated in Figure 2.12.

![Figure 2.11 Relationship of shear stress and shear rate of TiO₂ dispersion of different volume fraction [119]](image-url)
Another factor that would be considered as determiner of suspension rheological behaviour is the size of dispersing particles. In Figure 2.13, Barnes [85] used regression to show the relationship between particle size and critical shear rate. It is a clear representation of decreasing critical shear rate with the increase of particle size. Furthermore, in a more systematic study, Maranzano and Wagner [120] performed studies on a series of chemically similar, monodisperse silica spheres dispersed in an accurate study of the effect of particle size on shear thickening. The result presented in Figure 2.14 shows the value of the critical shear rate they obtained for a number of suspensions with different size particles at different weight fractions, which demonstrates the particle size dependence of critical shear rate of STFs.
Although the mechanism is not fully understood, particle shape has also long been known to cast effect over the shear thickening behavior.

It is found in the coatings industry that clays and precipitated crystalline dispersions may exhibit shear thickening [85]. A model system studied is precipitated calcium carbonate dispersion (Figure 2.15) which shows shear thickening behaviour resembled to typical spherical particle suspensions as shown in Figure 2.16 [121].
Through advanced Rheo-SANS measurements [93], it was demonstrated that the rod-shaped particles assume and maintain aligned direction of flow field in shear thickening regime, which ruled out an earlier assumption that shear thickening phenomenon came from flow caused misalignment [122]. Generally speaking, particles with clear anisotropy will demonstrate shear thickening at lower fractions than typical spherical particles.

Figure 2.15 microscopic observation of rod-shape precipitated calcium carbonate [118]

Figure 2.16 steady shear behaviour of precipitated calcium carbonate dispersion
that exhibits shear thickening effect [121]

As stated in previous subsection, a typical STF must not be flocculated before shear loading is applied, thus it makes particle-particle interaction a very important issue in adjusting STFs behaviour, as there must be no net attraction between particles. Several stabilisation mechanisms have been introduced to achieve the discrete phase of STFs, for instance electro-static repulsion and/or steric repulsion achieved by surface modification of dispersing particles. Consequently, rich non-linear rheological behavior may be realised through these particle processing.

As investigated by Laskowski [123], shear thickening phenomenon may be avoided with a hydrophobic silica particles dispersion, which was generated by replacing surface silanol groups of typical fumed silica particles with methyl groups.

Maranzano et al. [124] systematically studied the effect of surface charge on shear thickening behavior of an example dispersion of 3-(trimethoxysulyl)propyl methacrylate (TPM) coated colloidal Stöber silica particles through advanced techniques of zeta-phase analysis light scattering and small angle neutron scattering.

The effect of external field, electrical or magnetic, on STFs has recently drawn attention, as this would realise the possibility of actively harnessing the shear thickening behavior. Brown et al. [125] studied the generality of shear thickening phenomenon and reported that shear thickening could be masked by a yield stress and could be recovered when the additional yield stress decreased below a threshold value. The yield stress could be particle interaction or field induced force such as magnetorheological force and electro-rheological force. In light of this, Shenoy et al. [126] reported an electrical responsive shear thickening fluid, generated by dispersing surface engineered silica particles in organic solvent, 4-methylcyclo-hexanol. A mechanism was also proposed indicating how electrical field could suppress the formation of hydro-cluster microstructure, which led to delaying of shear thickening and increased critical shear stress by the same author.

Zhang et al. [127] presented a magnetorheological counterpart, and clearly defined effective packing fraction of field sensitive dispersing particles for the coincidence of shear thickening and magnetorheological behaviour.


2.3.5 Shear thickening mechanisms

The research of investigating the microstructural affined mechanism at the onset of shear thickening behaviour has been vigorous in the past decade with the application of new experimental techniques that have the ability to probe the dynamic structures in situ, as the shear thickening dispersion is being sheared. For instance, Maranzano et al. [128] developed the method of ‘Rheo-SANS’, which involved x-ray and neutron scattering techniques, to study the microstructural evolution of colloidal silica dispersion at the onset of shear thickening transition. Confocal microscopy on the observation of individual particles was also applied by Cheng et al. [88] to study the mechanism of shear thinning and shear thickening phenomenon. With the advance of computational power, simulation method is capable to calculate considerable particle numbers and system sizes, so as to reveal the microstructural evolution that leads to non-linear rheological behaviour at the particle level [87, 129, 130].

Three types of mechanisms that are widely accepted, which are, namely, order-disorder transition (ODT), hydro-cluster and dilantancy, respectively.

Order-disorder transition

The first widely identified mechanism for the shear thickening phenomenon is the ODT developed by Hoffman [131, 132]. This theory argues that colloidal particles would take a regulated structure into layers or strings, due to well flowed status of the dispersion at low shear rate. For instance, an ordered hexagonally packed layers could be observed prior to the stage of shear thickening phenomenon for a number of polymer particle suspensions [117, 131, 132]. Besides, the relative motion of these layers are considered as the reason of temporary shear thinning regime under low shear rate, which is a coincidence of general behavior of STFs. However, with the increase of shear rate, the lubrication forces between particles would increase fast and lead to rotation of the stable structures, thus cause misalignment of the orderly pack and destabilised flow. Then, the shear viscosity is expected to increase dramatically, due to an increase in inter-particle interaction caused by the dismantling of the orderly structure. Consequently, a disordered state of the dispersing particles could be
observed during the course of shear viscosity increase upon shear rate increase. Through the techniques of small angle neutron scattering (SANS), Laun et al. [96] was able to provide experimental evidence of the ODT following Hoffman’s work. This framework of the ODT was successful, as Hoffman et al. [132] and Boersma et al. [133] were able to formulate physical models based on the balance between shear force and inter-particle interaction, which predicted the critical shear rate precisely at the onset of shear thickening.

Despite the fact that the order-disorder mechanism successfully predicted the critical shear rate of shear thickening effect, it has been shown definitively that shear thickening could occur without an order-disorder transition [133,121]. Thus, while the order-disorder transition is a possible way to explain shear thickening behaviour, it is not a required mechanism.

*Hydro-cluster*

Since the proposal of the order-disorder explanation, simulation and experimentation studies have been flourishing, and led to a better perceived explanation, which states that reversible shear thickening results from the formation of hydro-clusters.

The hydro-cluster mechanism was firstly introduced by Brady and Bossis in 1985 [134], who proposed that the dispersing particles were pushed into close proximity by shear loading, thus in order to move away from each other, neighboring particles must overcome large viscous drag from the small lubrication gaps. When the shear rate was applied at a small value, the particles were moving independently. However, with the growing shear rate, a critical value was expected to cause the particles sticking together by lubrication forces; and this would lead to shear induced self-organisation of the dispersing colloidal particles. As shown in Figure 2.17 [86], with the continual increase of shear rate, separate particles were then forced into close proximity which formed hydro-clusters. Consequently, the movements of the dispersing colloidal particles were no longer independent to each other, thus it would result in larger aggregates which could eventually jam the flow.
This mechanism of hydro-clusters has been successful since it could reproduce shear viscosity curves that matched the measurements for continuous shear thickening, in terms of both the critical shear rate and the magnitude of the increase of shear induced viscosity [135-137]. Furthermore, confocal rheology measurements have come to a direct evidence through observing hydro-clusters coinciding with the shear thickening behaviour [88], as shown in Figure 2.18. This improved understanding of shear thickening mechanism allows the development of a model to predict the critical stress at which shear thickening occurs based on the particle size and interaction potential between particles, which has been verified through experimentation [120].

Even though the hydro-cluster model agrees with experiments for a wide variety of continuous and discontinuous shear thickening systems, it has some difficulty in producing shear viscosity increase larger than a factor of 2, which is much less than the experimental observation of higher packing fractioned shear thickening systems that generally demonstrate DST. Thus, it leads to some doubt of hydro-clustering mechanism being able to reveal the entire picture of shear thickening, and possibility of the co-existence of other mechanisms in shear thickening, especially the discontinuous type.
Dilatancy

The attempts of explaining shear thickening behavior through the formation of hydro-clusters, which attribute effective viscosity increase to the lubrication drag forces at the gaps between particles, have encountered some difficulty in explaining the steep viscosity increase in DST, as even the upper limit of simulation and calculation proves to be less than actual experimental facts at the onset of DST. As a result, dilatancy, which featured dense granular flows, is also adopted as a mechanism for shear thickening, as dilatancy is often observed with the DST [119]. According to a number of experiments, dilatancy is related to increase of volume of densely packed particles dispersions that are subjected to increasing shear loading [95], thus leading to additional coupling stresses that is proportional to normal force out of frictional (solid-solid) contacts on the boundaries of the confinements. This force usually transmits interiorly along force chains which would grip the dispersion together at a steady state without letting the dispersing particles drifted away from medium fluid during DST, which enables dramatic shear viscosity increase with shear rate increase. With the knowledge of dilatancy, models have been developed quantitatively to predict stress profile of shear thickening regime. Even though it still could not precisely fit the slope of the shear viscosity curves, it is able to explain the normal force measurements during DST, and to reveal the dependence of DST on various boundary conditions [18, 95, 115, 125].
2.3.6 Applications of STFs

STFs bear huge interest in industrial applications; large numbers of patents are issued to both specific applications and preparation of novel STFs. For instance, a shear thickening fluid used in conjunction with fabrics was proposed for utilisation in an expandable spacecraft [138], which combined the fluid and the fabric to resist penetration of hypervelocity particles in space.

The potential applications for STFs include pads for sport equipment. A mouth guard for improved energy dissipation are proposed as well, which would reduce the likelihood of concussion or dental damage.

Other applications proposed are protective wears, including gloves for reducing vibration or protecting the hands from jarring impact, as well as sports shoe designs for energy dissipative construction.

Composites comprised of discrete droplets or co-continuous networks of STFs could also be applied in seat cushioning and neck supports in automobiles, planes and trains to provide better protection in case of accidents. Shear thickening materials could be applied where the stiffness or hardness of a flexible component could change as a result of deformation, such as from elongation, bending, torque, twisting, or compression. The materials could be used as a medium to control mechanical actuation of one object relative to another [100].

Three main application streams of STFs application featuring adaptive stiffness and damping, smart structures and body armor, will be reviewed in more details in following paragraphs:

Adaptive stiffness and damping

With the ability to undergo dramatic shear stress response and increased energy dissipation ability automatically when being subjected to the change of external shear loading, STFs may be considered as a promising candidate for the fabrication of viscoelastic damper, which provides adaptive stiffness and damping. Jolly et al. [139] proposed a viscoelastic damper featuring STFs, which could mitigate vibration of structural facilities under disastrous scenarios, such as, earthquake or strong wind.
Zhang et al. [92] evaluated the dynamic performance of a small scaled damper filled with STFs, which provided systematic benchmarks for prototype fabrication of STF involved damping devices.

**Smart structures**

The fast and reversible property change of STFs could also be applied to the so-called smart structures, which realise handy designs of industrial products. STFs are mentioned to be used as a tamp in controlled pulse fracturing (CPF) [140] to minimise the damage to the downhole equipment. STFs are expected to become more viscous and more resistant to flow when experiencing increased velocities due to the force generated by ignited propellant, which would slow down or even stop the upward movement of structures thus rule out the possibility of any damage that might be caused.

Helber et al. [141] proposed a passively switchable STF mount for industrial machinery with the function of vibration attenuation. The authors claimed that this mount controlled displacement in vibrating system with one degree of freedom. Fisher et al. [142] invented composite structures with tailored stiffness and damping performance with the application of STFs, which may be advantageous in sports equipment, aeronautics, aerospace and other consumer goods where requires tailored dynamic properties. Beside, these industrial applications, STFs related devices are also developed for medical equipment to alleviate sudden movement of human joints such as shoulder, knee, elbow, ankle, hip, etc., so as to prevent the patient from contusion. STFs are also used for surgical and medical garments to inhibit penetration of garments. Williams et al. [143] reported that the puncture resistance was increased when STFs were incorporated into surgical garments such as surgical gowns, surgical gloves, surgical masks and other wound-care products and the like, where the STFs were used as a layer on at least one of the inner and outer surface of the garment.

A multi-layered STF composite was prepared for stopping projectiles by Joanna et al. [144]. This composite included a stack comprised of mesh and STF layers that were able to resist the impact of projectiles or bullets. Wasserman et al. reported recently [145] that shear thickening compositions could function in an energy or
communications transmission cable to provide enhanced protection against unexpected external forces, e.g., cutting or puncture from a shovel. The shear thickening composition not only provided protection against mechanical damage but also enhanced the cluster formation mechanism for superior flame retardness that were better than existing technologies.

**Body armor**

Till now, the most important application with STFs is human protection kit. Effective body armor should not only provide adequate protection against prevailing threats, but also sacrifice minimum level of wearers’ ability to perform, thus significantly broaden the area of human activity. Comparing to traditional body armors, which are stiff and bulky and lack of the ability of whole body protection, the recent trend of STFs based liquid body armor could be a much more flexible and yet effective option. Large number of inventions and methodologies have been achieved in this fruitful field of research.

Cwalina et al. [146] reported improvement on standard extra-vehicular activity (EVA) suit by replacing traditional filler materials with absorber layers that integrate STF intercalated Kevlar® armor. This invention was tested for efficacy against both needle puncture and hypervelocity impact (HVI) mimic of micrometeoroids and orbital debris (MMOD). Turned out the STF-kevlar® featured EVA suit showed an improvement in puncture resistance tests to standard EVA suit that adopted neoprene-coated nylon as filler, whistle being 17% thinner and 13% lighter than its counterpart. Thus, this work demonstrated a meaningful method dealing with MMOD threats.

Park et al. [147] compared ballistic resistance performance of STF impregnated Kevlar® fabric with neat Kevlar® fabric in a high velocity projectile tests, where a 2 stage light gas gun was used to generate speed as much as 1~2 km/s, so as to evaluate the protection performance of STF involved body armor in real battle situation. As could be deducted in Figure 2.19, STF impregnated Kevlar® exhibit approximately 70% improved energy absorption in terms of volume areal density and fabrication material cost over neat Kevlar®.
Fowler et al. [148] proposed to use shear thickening nanocomposites as impact resistant materials to provide protection against concussions and other impact related injuries. An Instron\textsuperscript{TM} drop tower was used to investigate the difference in peak forces and accelerations between the prototype with STF nanocomposite and standard impact foam from commercial football helmet for low kinetic energy impact. Significant reduction in peak force and acceleration was recorded for STF nanocomposite involved sample with acceptable sensitivity, which suggested that STF nanocomposite materials were a promising candidate of novel energy dissipating components in personal protection gears.

Petel et al. [149] studied particle strength and volume fraction difference on the ballistic performance of pure STFs by shooting a chisel-nosed projectile into capsules containing different dispersions. It was found that particle strength should also be considered as a factor in determining the resistance of inter-particle stresses upon impact as well as the well-known volume fraction. A harder particle generally demonstrated better performance in this regard.

Harris et al. [150] investigated the shock wave mitigation of STF impregnated fabric
composite under ballistic impact experiment. It was found that the normalised average peak pressure amplification was significantly reduced from 2.46 to 1.49 while the attenuation in normalized maximum rate of pressure rise was even more pronounced from 2.3 to 0.76 after STF treatment, a satisfactory outcome that justify the ability of wave mitigation for STF composites.

2.3.7 Conclusion

This subsection presents a review of the state of the art in STF research revealing a growing need to understand all aspects of STFs, to model their behaviour and to improve their applications by optimising components and fabrication procedures. This review shows that there is significant research in progress that is continually developing new STFs with new carrier fluids and/or particles, optimised conditions or novel manufacturing techniques to meet new and more demanding requirements.

2.4 Ionic liquids and their applications

2.4.1 General description of ionic liquids (ILs)

Ionic liquids (ILs) have been known for over a century, since the first synthesis in 1914 by Paul Walden [151]. However, little attention was paid to the primitive ILs, as these ILs required high working temperature (150-1000°C), as well as being corrosive and highly active for reactions [152]. In 1970s, room temperature ionic liquids (RTILs) were developed with the discovery of alkylpyridinium or 1,3-dialkylimidazolium haloaluminate salts [153], which led to the first electrochemical studies concerning the newly developed ILs [154]. Unfortunately, these haloaluminate ILs are highly sensitive to moisture and require special attention to prevent the hydrolysis. It was not until 1990s, when new generation of RTILs were invented with the introduction of the first few kinds of air stable ILs 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF4]) and 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF6]) featuring organic ions, the study of ILs started to progress on a rapid
track, and the number of air and water stable ILs soared [155]. Unlike their haloaliminate counterparts, this new generation of RTILs possessed much improved stability, and could be prepared, stored, handled outside a glovebox. Besides, by tuning the cations and anions combinations, variety of ILs may be customised according to specific applications, thus being considered as magical chemical due to the outstanding versatility [151]. With the above description we could come to the updated definition of ILs following the continual development of this fascinating material of ILs: Ionic liquids are room temperature molten salts composed of organic ions that may undergo almost unlimited structural variations [156].

2.4.2 Properties of ILs as electrochemical solvents

Due to their unique combination of physiochemical properties, for instance, negligible vapor pressure, non-flammability, prominent chemical, thermal and electrochemical stability, optical transparency and high conductivity, ILs have received considerable attention in electrochemical applications. In this subsection, the evaluation of ILs as potent electrolyte material is reviewed through different prospective, including viscosity, conductivity, solvent properties and electrochemical window.

2.4.2.1 Viscosity

Viscosity of liquid electrolytes is an important parameter, as it poses strong effect on the rate of ion transportation, as well as the conductivity. Previously, viscosity is generally considered a drawback for the application of ILs in electrochemical systems, as ILs are viscous liquid possessing viscosities 1-3 orders of magnitude higher than conventional liquid electrolytes [157].

For a specific cation, the shear viscosity of ILs is dependent to the size, shape and molar mass of the anions. Generally speaking, ILs with smaller, lighter and more symmetric anions possess increased viscosity. For example, the ILs with lowest viscosity contain large bis(trifluoromethane)sulfonimide [TFSI] anion, while the most viscous ILs contain Hexafluorophosphate ([PF₆]⁻) anion. However, Van der Waals
interactions and H-bonding are proved to have pronounced effect on viscosity, as increased Van der Waals interaction and/or H-bonding would lead to unexpected increase in viscosity [158]. For example, ILs containing bis(perfluoroethylsulfonyl) imide anion ([BETI]) are more viscous than ILs containing relatively smaller bis(trifluoromethane)sulfonimide anion ([TFSI]). The influence of cations on the viscosity of ILs is determined by the chain ramification of alkyl unit, the longer chain length and the more complex alkyl chain branching, the more viscous of the corresponding ILs, due to stronger Van der Waals interactions and ease of H-bonding formation. This trend could be confirmed by the example that the viscosity of 1-isobutyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide is more than three times of the viscosity of 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide. Moreover, with the increase in temperature, significant decrease of viscosity is generally observed [159].

2.4.2.2 Conductivity

Conductivity is the most important factor in determining the potential of applying ILs to any electrochemical process. Being composed of entirely ions, the ILs exhibit high conductivities with all these charge carriers. To date, the ILs exhibit conductivity in a range between 0.1 to 20 mS/cm [160]. A few exceptional examples of ILs with tricyanomethanide anion and the dicyanamide anion possess conductivity up to 36 mS/cm [161, 162]. The major determiner of the conductivity is viscosity with an inverse linked relationship. Thus, the ILs containing [TFSI] is a class that considered most conductive, due to their low viscosity [160]. Besides, several other factors also contribute to conductivity of ILs, namely ion size, anionic charge delocalization, density, aggregation and correlated ionic motions [161].

2.4.2.3 Solvent properties

Considering the complex composition of ILs with nearly unlimited combination of
cations and anions of different structures, there exists a maneuver of complex interplay of forces, for instance, electrostatic force, Van der Waals interactions, H-bonding and possible $\pi-\pi$ stacking, which all contribute to the solvation ability of the ILs. Consequently, comparing to conventional organic solvents, ILs possess several advantages as summarised by Keskin et al. [163]:

- Wide adoption to dissolve many different organic, inorganic and organicmetallic materials
- ILs exhibit moderate polarity
- ILs consist of loosely coordinating bulky ions.
- ILs do not evaporate since they have very low vapor pressures
- ILs are thermally stable, approximately up to 300 °C.
- Most of ILs have a liquid window of up to 200 °C which enables wide kinetic control.
- ILs are immiscible with many organic solvents.

Beside the well-known environment friendly properties like non-volatile, non-explosive, recycle, the most fascinating feature of ILs as solvent is their ability to customise for specific properties for particular needs.

2.4.2.4 Electrochemical window

The electrochemical window, which is due to the oxidation of the anions and the reduction of the cations, are responsible for the anodic and cathodic limits observed in the ILs. The electrochemical window is thus determined as the potential at which the processes start [164].

ILs generally exhibit wide electrochemical window, as an inherent property of the cations and anions used for their preparation. This redox-robustness is desirable in applying them as electrochemical solvents and even replacement to current organic liquid electrolytes. The typical window for ILs is 4.5-5 V, with the specific case of [BMIM][BF$_4$] and [BMIM][PF$_6$] being up to 7 V [165].
2.4.3 Application of ILs

The research of novel ionic liquids is a new field, yet it is growing rapidly with numerous potential applications. The specific application areas can be listed as solvents for organic, organometallic synthesis and catalysis; electrolytes in fuel and solar cells; lubricants; stationary phases for chromatography; matrices for mass spectrometry; supports for immobilisation of enzymes; liquid crystal in separation technologies; templates for synthesis nano-materials, materials for tissue preservation; preparation of polymer-gel catalytic membranes and generation of highly conductive materials [155].

As pointed out by Abbott & McKenzie [166], ILs could be revolutionary media for electrodeposition of metals and semiconductors for their outstanding solvent ability, wide electrochemical window and negligible vapor pressures, which allow the robust influence over the morphology and crystal size of various metal deposits at a temperature well above 100 °C. By using ILs, it allows many impossible process in water bath viable and solve the toxicity issue with the traditional cyanides involved aqueous systems.

ILs have proved their value in semi-conductor electrodeposition as well. Al-Salman et al. [167] fabricated photoluminicent Si_{x}Ge_{1-x} with a bandgap of 1.5-3.2 eV through electrodeposition method from ultrapure ionic liquid containing silicon and germanium halides. Another significance in this study is that it readily proves that ILs could be used to generate deposits with such high purity that allows photoluminescence effects. Besides, it may indicate an economic method in the fabrication of solar cells.

ILs have already proved their importance in the field of energy storage and management systems. Large quantities of ILs involved electrolytes and electrochemical systems are developed every year. To name but a few examples: Wang et al. [168] reported a BMIMBF_{4}/γ-BL mixture used as electrolyte for Li/LiFePO_{4} cell. The proposed electrolyte is tested through viscosity, conductivity and thermal stability investigation, the result indicates that when the volume mixture ratio
is 40/60, the electrolyte exhibits high conductivity of 10.76 mS/cm at 25 °C, low viscosity and high thermal stability. Moreover, through the linear sweep voltammetry, the electrolyte exhibits wide electro chemical window of up to 5.3 V.

The physical and electrochemical properties of a family of organic-inorganic hybrid electrolytes based on the ionic liquid 1-methyl-3-propylimidazolium bis (trifluoromethanesulfone) imide covalently tethered to silica nanoparticles (SiO₂-IL-TFSI) were also investigated by Nugent et al. [169]. Without compromising lithium transfer number, the ionic conductivity displays prominent maximum with the addition of LiTFSI, especially when the mixture ratio is 13.4 wt% LiTFSI, the conductivity was enhanced by over 3 orders of magnitude relative to either of the mixture components. Besides, the hybrid electrolyte SiO₂-IL-TFSI/LiTFSI is thermally stable up to 400 °C and the electrochemical stability was as high as 4.25 V, which was a very attractive level.

Different from the above two examples of liquid electrolytes, the application of IL-based solid electrolytes for electrochemical devices such as fuel cells and dye-sensitized solar cells (DSSCs) is also of great interest. Gratzel et al. [170] reported high-performance DSSCs using a solidified IL electrolyte based on the gelation of an iorganic colloidal dispersion in an IL.

Besides the IL based electrolytes reported, large number of functional materials are derived considering the solvent nature of ILs.

A novel class of ionogel, which is essentially an ionic liquid-tethered nanoparticle suspension, was proposed by Moganty at al. [171]. The gel was fabricated by having silica nanoparticles densely grafted with [SpmIm]TFSI and having the tethered sample mix with the base IL BmpyrTFSI. Stable suspension was observed over the entire range of nanoparticle volume fraction. Also, the addition of silica-[SpmIm]TFSI was able to suppress crystallisation of the original IL base. This derived hybrid gel exhibited liquid-like transport properties over large temperature range.

ILs may be applied as electromechanical actuators, which show reversible deformation upon the application of voltage. These actuators could play the role of
artificial muscles for biomechanical and biomimetic applications. According to Lu et al. [172], who pioneered the application of ILs in electromechanical actuators, ILs could improve the actuators performance dramatically with an operational life easily surpass $10^6$ cycles.

### 2.4.4 Conclusion

In this subsection, the background knowledge of ionic liquids is reviewed from different prospective of research history, basic property, synthesis and applications. Through the description of the context, it is revealed that the adoption of ionic liquid as medium for the generation of new functional compact materials is a new yet intensively studied field. The rheological study of this new breed of materials, which shed a light on the mechanical response of the integrated materials, should open another door for the further application of both the ionic liquid itself and other novel multi-functional materials.

### 2.5 Summary

In this chapter, the up to date knowledge concerning magnetorheology, shear thickening and ionic liquids are substantially reviewed from the aspects of material compositions, operating mechanisms, rheological behaviors, phenomenological models and applications. With the rich context of all these knowledges, brand new materials may be designed with combined advantages through the hybridisation of different concepts. Such research may be beneficial effort in characterising the novel materials for various working conditions, and lead to much more applications in multifunctional smart devices and structures.
Chapter 3 Experimental and Modelling Study of Viscoelastic Behaviors of Magnetorheological shear thickening fluid (MRSTF)

3.1 Introduction

As is systematically review in previous chapter, Magnetorheological Fluids (MRFs) refer to the kind of fluids containing two phases of micro-sized ferro-magnetic particals and a carrier fluid, whose mechanical behavior can be manipulated by an external magnetic field. When the material is subjected to the external magnetic flux densities, the apparent viscosities for typical MRFs can increase as high as several orders of magnitude in matter of milli-seconds. And Shear thickening fluids (STFs) are functioned by concentrated colloidal suspension in fluids, which increase sharply with shear viscosity when the applied shear rate is beyond a critical point, where the increased shear viscosity is observed as both passively activated as well as reversible. Featuring respectively proactive and reactive control of their mechanical properties, MRFs and STFs are both well adopted in actual applications. The task here is to systematically study the viscoelastic properties of the novel magnetorheological shear thickening fluid (MRSTF) that combines both class of smart materials, so as to find a derivative showing both advantageous properties and introduce magnetic field control to the passive activated STFs. The field dependent properties of MRSTF is exploited through both steady and oscillatory rheological tests, and modeling approach is also applied to numerically simulate the properties of the proposed MRSTF.

3.2 Experimental setup

3.2.1 Fabrication of both STF medium and MRSTF

The STF is used as the base material, where it is composed of hydrophilic fumed
silica (S5505, from Sigma-Aldrich used as received) of a primary size of 14 nm and 
carrier fluid of ethylene glycol [HOCH₂ CH₂OH] (102466, ReagentPlus, from 
Sigma-Aldrich). In the fabrication process, the carrier fluid is added to the fumed 
silica powder and mechanically stirred for approximately 2h. After the stirring, the 
dispersed sample is placed in vacuum oven for several hours to eliminate air bubbles. 
In this case, a 25% wt fraction sample is selected for study.

Carbonyl iron particles (C3518, from Sigma-Aldrich) with 5 μm mean particle size 
are added to the prepared STF base to generate target MRSTF samples, the sample 
fraction generated is chosen as 5% [127], as the higher iron particle fraction would 
result in dominant MR behavior. The iron particles are mixed with STF and have the 
mixture manually stirred for 10 min, then the air bubbles are removed in a vacuum 
oven before tests are launched.

Through this fabrication process introduced above, the MRSTF sample is generated in 
a very stable form, and no supernatant or phase separation could be observed even 
after a few months.

### 3.2.2 Rheological testing setup

A parallel-plate stress controlled rheometer MCR 301 is used with a constant gap of 
0.5 mm, by which steady and dynamic oscillatory shearing excitation is applied to the 
tested samples that filled the gap between two plates. An electromagnet attached to 
the rheometer is used to generate magnetic field, perpendicular to the shear flow 
within the gap. The magnetic flux density is applied and controlled by excitation 
currents following the conversion of B=220I (mT). In order to eliminate the pre-shear 
history and to distribute the particles evenly, a pre-conditioning shear is conducted 
prior to each test run. The pre-conditioning run is a constant shear of 10 s⁻¹ under zero 
field condition for 1 minute, and specific constant magnetic field is also applied to 
activate the liquid material. The magnetic field remains active during all the shear 
tests, as so to determine the field-induced mechanical properties.
3.3 Experiment results

3.3.1 Steady shear test of MRSTF

In order to compare the ability of shear thickening of the original medium (the shear thickening mixture of 25% wt silica in ethylene glycol base) as well as the effect of the addition of iron particles, the steady shear experiments were conducted on both the base fluid and the fabricated MRSTF in a stress sweep manner, where shear stress is applied to the tested samples and sweeps from 0.1 to 30000 Pa, shear viscosity values are then recorded. Figure 3.1(a) gives the shear viscosity-shear stress relation of original shear thickening fluid medium tested within different geometry. From the figure, it could be found that the shear viscosity of the shear thickening base fluid exhibited obvious upsurge upon a critical stress value. Besides, same experiments over the same original shear thickening fluid medium are found to exhibit great repeatability, when varied gaps between the parallel plates of the rheometer are adopted, thus eliminating inertial as possible reason for the increase of the shear viscosity. This result agrees with the countless publications which have already reported such an experiment outcome. The shear rate vs. shear viscosity curve is also presented in Fig. 3.1(b) assuming different gap values, which demonstrates a conformed result to Fig. 3.1(a).
Now that the steady shear response of the original STF is examined and confirmed, the effect of the iron particle addition should also be scaled. As it is given in Figure 3.2, the relationship between shear stress and liquid shear viscosity under augmented magnetic fields is presented. We can see that when the magnetic field is absent, the curve of the MRSTF could exhibit shear thickening behavior at nearly the same critical shear stress point as the original STF, despite the fact that the addition of iron particles might down-scale the actual values. And the augmented external magnetic field flux densities lead to increased shear viscosity in several orders of magnitude comparing to zero field condition at pre-yield region, before the onset of shear thickening behavior. Besides, with the increasing external magnetic field, as observable from the chart, the onset of shear thickening commence points is pushed to higher stress values. Moreover, the curves of different field conditions could always rejoin the zero-field curve after a minimum shear viscosity is exhibited with a smaller range of overlapping as the magnetic density increases. The experiment’s result revealed the fact that the attractive magnetization dipolar force could be applied to mask or control the onset of the shear thickening behavior, as additional yield stress is triggered due to magnetorheology as well as providing a source MR effect [125]. This phenomenon is staged by our MRSTF samples at wide range of the controllability of
Chapter 3 Viscoelastic Behaviors of MRSTF

shear thickening behavior, as it is revealed in Figure 3.2 that similar behavior is observed up to magnetic saturation point. With that we could come to the conclusion that the MRSTF being discussed here shows the dual function of magnetorheology and shear thickening, and the magnetic sensitive iron particles in this system provides us with a pathway to maneuver the shear thickening behavior by applying various magnetic field flux densities. In the following subsections, we would unfold the discussion to show dynamic situations as well as presenting the viscoelastic property of MRSTF under different variables like strain amplitude, frequency and external field through the LAOS test.

![Figure 3.2. Stress Sweep of 5% wt MRSTF under varied external field conditions](image)

3.3.2 Dynamic oscillatory shear test of MRSTF

3.3.2.1 Introduction of oscillatory test

Materials would display viscoelastic properties; one of the essential experimental schemes that examine the viscoelasticity is small amplitude oscillatory shear (SAOS) which provide rich and accurate rheological characterization for complex fluids or soft materials with the accuracy range of commercial rheometer. Although linear viscoelasticity is useful in interpreting the relationship between microstructures and rheological properties for viscoelastic material, it should bear in mind that the deformation is quite small within the scope of SAOS test. Therefore, large amplitude
oscillatory shear (LAOS) testing should reveal a different aspect of material behavior, as the deformation is extended to nonlinear regime, thus it is of more interest in the study of nonlinear viscoelasticity in suspensions.

The viscoelastic mechanical properties of materials can be systematically investigated by subjecting the sample to oscillatory deformation. This testing procedure allows for the opportunity to explore the viscoelastic properties in nonlinear regime and relate to steady flow and linear viscoelasticity within a 2-D experimental space defined by strain amplitude \( \gamma_0 \) and angular frequency \( \omega \). Additionally, the oscillatory shear does not involve sudden jumps in speed or position and it is therefore an easy flow to generate [173].

In oscillatory shear deformation, required input of shear strain takes the form of

\[
\gamma = \gamma_0 \sin \omega t
\]

Consequently, the oscillatory strain rate is given as

\[
\dot{\gamma} = \dot{\gamma}_0 \cos \omega t
\]

In this subsection, the experimental investigation of viscoelastic properties of MRSTF is launched through oscillatory shear flow under both strain and frequency sweep mode. The effects of strain amplitude and angular frequency on storage modulus, shear modulus are discussed. Also, the significance of macro experimental phenomena in microstructures is detected and illustrated.

### 3.3.2.2 Strain amplitude dependence of MRSTF

In the oscillatory strain amplitude sweep test, storage (G’) and loss moduli (G”’) are investigated under varied external magnetic fields with the strain amplitude sweeping from 0.01% to 100% at a constant frequency value of 5 rad/s. The experimental curves of MRSTF sample are shown in Figure 3.3.

From Figure 3.3, it is observed that the dynamic parameters for MRSTF without magnetic field is quite different from the occasions when the magnetic fields are applied, an obvious MR effect is displayed with a pronounced increase of several orders of magnitude.
Moreover, storage modulus \( G' \) for the MRSTF sample (Figure 3.3 (a)) without external magnetic field is constant for a large range of strain amplitude variation till approximately 10% before a slight decrease could be recorded. As for the occasions where magnetic field is applied, \( G' \) of the MRSTF sample displayed relatively shorter periods of plateau before starting to decrease at small deformations with the increase of external magnetic field. A series of critical strains, here defined as \( \gamma_c \), are thus used to signal the plateau periods of the MRSTF sample at different external field intensities, as could be noticed in Figure 3.3 (a).

This is to say the strain dependent viscoelasticity of the MRSTF sample was sensitive to external field condition, which is considered to be a consequence of the dismantling of particle chains when strain deformation is beyond a critical strain value of \( \gamma_c \), which is used to signal the transition point of LVE and NLVE range for viscoelastic materials. When the actual deformation falls in the range from zero to specific critical strain \( \gamma_c \), the microstructure of viscoelastic material is considered stable and intact, thus exhibits constant \( G' \) value. Conversely, when the strain amplitude is higher than this LVE range, the microstructure is destroyed and the NLVE regime is shown. The loss modulus \( G'' \) of the MRSTF sample also exhibits a plateau for small strain amplitudes, and then it increases steadily to a local maximum value before it decreases gradually, as it is shown in Figure 3.3 (b). The dynamic property of MRF generated in same fraction is also summarized in terms of storage modulus (\( G' \)) and loss modulus (\( G'' \)), as given in Figure 3.3 (c) and (d). It is observed that the MRF sample demonstrates reduced LVE range comparing to MRSTF. Besides, the MR effect of MRF exhibits quicker saturation comparing to MRSTF counterpart, as obvious overlapping of modulus curves could be noticed at relatively high magnetic field intensities.
Figure 3.3 (a) $G'$ and (b) $G''$ variation with strain sweep range 0.01-100% at 5 rad/s angular frequency for MRSTF sample; (c) $G'$ and (d) $G''$ variation with strain sweep range 0.01-100% at 5 rad/s angular frequency for MRF sample
Comparing $G'$ and $G''$ of MRSTF, Figure 3.4 gives the strain amplitude sweep result in a single chart, where the applied external magnetic field is 220mT. It is observed that storage modulus decreases from small deformation, and the loss modulus increase to a local maximum before decreasing, a crossover point where loss modulus outweighs storage modulus is displayed at comparatively high strain amplitude. This behavior is not accidental, as other tests given in Figure 3.3 are found to present a conformed trend. This phenomenon is usually referred to as weak strain overshoot [55], and is connected to a typical MRF response in many ways [174].

The pronounced local maximum in loss modulus signals a remarkably robust feature of soft glassy materials, the MRF is categorized in such domain. If we consider modulus increase as a result of network formation and decrease as a consequence of network destruction, then the local maximum loss modulus means the balance between formation and destruction is more dominant in the formation aspect until the structure destruction parameter overtakes it. One plausible explanation given to the $G''$ overshoot is that the microstructure established at early oscillatory deformation is destroyed and reformed at high strain deformation [175]. What is also worth noting is that the MRSTF sample shows no thickening behavior, which should feature in both $G'$ and $G''$ increase at high strain amplitude. This is on one hand due to the fact that actual shear rate of oscillatory test is not so high to trigger the shear thickening phenomenon, and on the other hand is explained by the fact that the thickening
behavior is suppressed in the mixture system [92,125].

With what is mentioned above, we can conclude to a certain extent that the fabricated MRSTF samples behaved more like MRF under oscillatory test when the external magnetic field is applied.

The large amplitude strain shear test is also conducted through the analysis of stress-strain loop within one oscillatory cycle. It is proposed that the hysteresis loop for strain-stress would be elliptical in case of sinusoidal loading when the strain amplitude is within the LVE range, and gives rise to a non-elliptical shape due to higher harmonics distortion when the excitation is beyond linear viscoelastic (LVE) range.

The stress-strain loops of the MRSTF sample under different strain amplitude in a period when the external magnetic field is not applied are presented in Figure 3.5 (a). It is clear to see that the stress-strain loops for MRSTF without a magnetic field were elliptical in shape when the strain amplitude ranged up to 10%. This phenomenon demonstrates that the MRSTF could be referred to as LVE material within the strain range of 0-10%, which was a consistent result as is mentioned previously in a strain sweep test.

As a comparison, the LAOS test result of MRF is often presented in rectangular shape even at large strain deformation, as given in Figure 3.5 (b). It could be concluded that even though the MRSTF sample exhibits a lot property in common with typical MRF generated in same fraction (mixture of 5% wt iron particles and silicone oil), there are obvious differences. The current MRSTF material shows observable slopes with the ellipse loops, which demonstrates sound stiffness, while no such slope could be detected with MRF under zero field condition [176].
Furthermore, the strain-stress relationship of the MRSTF sample under the condition of external magnetic field is presented. From Figure 3.6 (a), we could see that when the strain is within the linear regime, as was found in the strain sweep tests, the strain-stress hysteresis loops exhibited an ellipse in shape, yet the area of the loop as well as the slope between main axis and x-axis maintained approximately the same value. This phenomenon indicated that when the material is deformed under LVE range and the damping capacity is not a function of external strain input and the stiffness is also independent of that very variable parameter. Therefore, it reflected a conformed result of constant moduli in linear range under the configuration of strain sweep tests. As for the MRF sample, the hysteresis loop was found to be effectively assembled due to the fact that the iron particles were forming a same gap-spanning structure and are not ruptured for both kinds of liquid samples within linear range, Figure 3.6 (b) demonstrates this.
Further comparison of the hysteresis strain-stress relationship of MRSTF is presented in Figure 3.7 (a), where the strain amplitudes are considerably larger and extended to NLVE range. From this figure it could be found that the stress response against strain amplitude could still maintain its elliptical shape when the scale was up to 6% before gradually deforming into an irregular shape, for instance, at the strain amplitude of approximately 15%. It is worthwhile pointing out that this set of hysteresis loops exhibit notable difference compared to the result presented in Figure 3.6, even though the loops appeared linear. It was observed that the slope between the main axis and x-axis decreased with the increasing strain amplitude and the area of loop increased with the increase of deformation, this phenomenon signals variable damping capacity and stiffness against strain amplitude under certain external magnetic field. The observed phenomenon means that the nonlinear behavior might not be observed immediately before the microstructure was completely destroyed. The MRSTF could still maintain linear response when the microstructure was partially destroyed even though the dynamic performance like storage and loss moduli have already shown significant effect upon the destruction of microstructure [57].

While in the case of the MRF, as could be found in Figure 3.7 (b), the loops for the MRF were approaching nearly the same rectangular shape under different strain deformations, which meant limited variation on stiffness in NLVE range.
Figure 3.6. Linear strain-stress relation of (a) MRSTF and (b) MRF under field condition

Figure 3.7 Transition of linearity and non-linearity for (a) MRSTF and (b) MRF under external magnetic field

With the description, we can conclude that the MRSTF possesses linear viscoelastic (LVE) range of 0-0.1%, even though an elliptical stress response could also be observed at an early stage of non-linear regime, which demonstrated that the very material was prone to maintain the linear response until initial microstructure is
completely destroyed. And the key criterion in deciding the actual transition point is to examine the strain dependence of damping capacity and stiffness of the material.

3.3.2.3 Frequency dependence of MRSTF

Apart from the strain amplitude examination, frequency is another factor that influences the dynamic rheological performance of viscoelastic materials. Figure 3.8 gives the frequency sweep test result for moduli comparison from 1-100 angular frequency at small constant deformation of 0.05%, which is within the linear viscoelastic range as shown in Figure 3.3. This figure shows that the storage modulus increased slightly with the increase of angular frequency, whereas the loss modulus remains more or less the same in the frequency sweep range. Also the storage modulus is higher than loss modulus in the entire range, which indicates that the MRSTF is of predominantly elastic response in the angular frequency range of 1-100 rad/s.

![Figure 3.8 Storage and loss modulus of MRSTF versus angular frequency when strain amplitude is 0.05% within LVE range, B=220mT](image)

Figure 3.8 Storage and loss modulus of MRSTF versus angular frequency when strain amplitude is 0.05% within LVE range, B=220mT

The effect of angular frequency inputs on MRSTF performance when the strain amplitude is beyond the LVE range is presented in Figure 3.9. In Figure 3.9, we can see that at low frequencies the storage modulus $G'$ exhibits an approximate plateau value until a certain frequency, then $G'$ decreases gradually with the increasing frequency. The frequency point at which $G'$ starts to decrease is defined as critical
Chapter 3 Viscoelastic Behaviors of MRSTF

With the frequency increasing further, \( G' \) displayed a local minimum at a frequency value \( \omega_m \), then started to increase again. In contrast the loss modulus \( G'' \) increases gradually until the frequency point \( \omega_m \), then starts to decrease. This phenomenon shares much similarity with MRF, and is also a direct evidence of microstructural variation of the MRSTF under different driving frequencies. The experimental can be explained in this way: When the frequency is low, the dynamic shear rate, which is defined as \( \omega \gamma \), is at very low level, thus the microstructure of the MRSTF did not experience obvious change. In this situation, the hydrodynamic forces could not be compared to chain-chain interactions that constitute the microstructure of MRSTF, thus the storage modulus \( G' \), which represents the elastic component of the viscoelastic material is of near constant value at small frequency ranges. When the frequency value increased to \( \omega_c \), the microstructure of MRSTF started to break due to the increasing dynamic shear rate, which caused the decrease of \( G' \). However, when the driving frequency was increasing to higher level, for instance \( \omega_m \), the oscillatory deformation was applied to the material at a fairly fast rate and that should leave limited time for the structure to either rearrange or break. Then the magnetostatic forces started to take dominant role in the microstructural interactions, and led to the fact that \( G' \) increased gradually after a certain frequency was surpassed. This experimental result once again confirms the conclusion that the MRSTF behaves quite assemble to MRF in the case of dynamic oscillatory shear.

![Figure 3.9 Storage and loss modulus of MRSTF versus angular frequency when strain is 1% which is in NLVE range, B=220mT](image)

**Figure 3.9 Storage and loss modulus of MRSTF versus angular frequency when strain is 1% which is in NLVE range, B=220mT**

From the point of Lissajous loop, which explains the hysteresis behavior of
viscoelastic materials. The stress-strain loops for MRSTF sample at different angular frequency when strain amplitude is 0.06%, which lies within LVE range, are represented in Figure 3.10. From this figure, we can see that the loops do not show much difference with either damping capacity or stiffness when the strain amplitude is within linear regime. This result provides sound proof with the frequency sweep tests described earlier.

The stress-strain loops for MRSTF sample at different frequency when strain amplitude is 1%, which falls in the non-linear range, are represented in Figure 3.11. From this figure, we can see that the loops do not show much difference with either damping capacity or stiffness with the variation of angular frequency. The elliptical shape was maintained until the angular frequency is at a relatively high level of 35rad/s, which is a compatible result with $\omega_c$ shown in Figure 3.9. Comparing the hysteresis loops of varied angular frequency within or beyond the LVE range, we can come to the conclusion that the material’s mechanical performance is independent of angular frequency change.

![Figure 3.10 Strain-Stress hysteresis loop of MRSTF sample under different frequency when strain is 0.06% which is within the LVE range, B=220mT](image)

Figure 3.10 Strain-Stress hysteresis loop of MRSTF sample under different frequency when strain is 0.06% which is within the LVE range, B=220mT
Figure 3.11 Strain-Stress hysteresis loop of MRSTF sample under different frequency when strain is 1% which lies beyond the NLVE range, B=220mT

3.3.2.4 Field dependence of MRSTF

The magnetic field dependence of MRSTF can be easily analyzed by setting the material at a fixed strain amplitude and driving angular frequency. Figure 3.12 gives the strain-stress loops of MRSTF under augmented levels of magnetic fields when the strain amplitude is set as 0.07% at a constant frequency of 5rad/s. It is seen from this figure that the slope of main axis and x-axis is dependent on the external magnetic field, while the overall shape as well as the area of hysteresis loops do not change significantly over the variation of magnetic fields. The experimental results reveal that the magnetic field is not the factor that introduces non-linearity and changes in overall damping performance, but was able to control the material’s stiffness within the LVE range.

Figure 3.12 Field dependence of MRSTF under fixed strain of 0.07% and frequency of 5rad/s
The field dependence of MRSTF when the strain amplitude is in the NLVE range of 1% under the oscillation of 5rad/s is given in Figure 3.13. From this figure, the loop shapes are all perfect ellipses, which is a consistent result that the MRSTF is able to maintain linear stress response before the microstructure is fully destroyed, when the external excitations either physical or magnetic are of intermediate level. Likewise, the experiment also indicates the result that the magnetic field could not introduce non-linearity, but is able to control the material’s stiffness and overall damping performance, which is comparable with the facts in the tests within the LVE range (Figure 3.12).

![Diagram](image)

**Figure 3.13 Field dependence of MRSTF under fixed strain of 1% and frequency of 5rad/s**

### 3.3.2.5 Modelling approach of MRSTF

*Four-parameter-viscoelastic model*

The experimental results, shown in previous subsections, indicate the relation between stress response and input strain amplitude as well as their strain, frequency and magnetic dependence. These descriptions reveal the viscoelastic properties of MRSTF.

Previously, the viscoelastic properties of MR and ER fluids were studied intensively through experimental and modeling approaches [177]. Compared with ER and MR fluid, the MRSTF material exhibits field dependent modulus and damping capability, thus a four parameter viscoelastic model developed which is [78] shown in Figure 3.14, which extends the classical three-parameter standard solid model, is applied to
model the rheological behavior of MRSTF.

**Figure 3.14. Four parameter viscoelastic model [78]**

In this model, \( k_1, k_2 \) and \( c_2 \) constitute standard viscoelastic solid model, which describes damping capacity of the model, while the field dependence of modulus is expressed in the parameter \( k_b \). The strain amplitude is \( \gamma \), and the response stress is presented by \( \tau \), the strain-stress relationship is given in Equation 3.3.

\[
\tau = (G' + iG'') \gamma
\]

where \( G' \) and \( G'' \) are respectively real and imaginary parts of complex modulus and can be derived in following method [178].

\[
G' = \frac{(k_1 k_2 + k_1 k_b + k_2 k_b)(k_1 + k_2)^2 + c_2^2 \omega^2 + c_2^2 \omega^2 k_2^2)}{(k_1 + k_2)(k_1 + k_2)^2 + c_2^2 \omega^2)}
\]

\[
G'' = \frac{c_2 \omega k_2^2}{[(k_1 + k_2)^2 + c_2^2 \omega^2]}
\]

In this set of equations \( \omega \) is the driving angular frequency of the oscillatory shear test, in which the input strain is in a harmonic form. For a harmonic strain input with an amplitude of \( \gamma_0 \), the stress response is obtained as

\[
\tau(t) = \gamma_0 \sqrt{G'^2 + G''^2} \sin(\omega t + \phi)
\]

where \( \phi \) is the phase lag between the input and output, which is calculated by

\[
\phi = \tan^{-1}(G''/G)
\]

**Parameter identification**

Based on the above equations, the relationship between strain input and stress output is established, and the moduli \( G' \) and \( G'' \), which are involved in the calculation, could be determined by fitting the four unknown parameters based on the method of least squares minimization on the platform of Matlab. In this optimization process, the
model-predicted stress is given by $S_m$ and the actual experimental data is $S_e$, and the objective function is thus proposed as

$$J = \sum_{i=1}^{N} (S_m(i)^2 - S_e(i)^2)^2$$  \hspace{1cm} (3.8)$$

Where $N$ is the number of experimental data in one loop. In the optimization process, the smaller the value for objective function, the more accurate the estimation for the parameters is.

Different sets of the four parameters were estimated for different experimental conditions. The parameter values for four different current inputs and constant strain amplitude of 1% are presented in Table 3.1. From the result of the identified results, all four parameters increase steadily with the increase of external magnetic field, which demonstrates field dependence same as shown in experimental results. Especially, the parameter $k_b$, which is related to the field dependence of modulus, increase from around 2kPa at 110mT to 5kPa at 440mT, the parameters evolution with respect to external magnetic fields are presented in Figure 3.15. From the curves given in these figures, the field dependence is clearly defined. This phenomenon demonstrated that the external field could alter stiffness of MRSTF material, and this is a conformed result to Figure 3.13.

With the resultant estimated parameters from the optimization process, we could also virtually reconstruct the strain-stress relationship and have it compared with the experimental data. The comparisons are presented in Figure 3.16. It is seen that the plots from the four parameter model can reflect the experimental results at different magnetic fields with acceptable accuracy.

| Table 3.1. Identified parameters for MRSTF with the input strain amplitude being 1% |
|---------------------------------|-----|-----|-----|-----|
| Strain Flux density | $k_b$ (kPa) | $k_1$ (kPa) | $k_2$ (kPa) | $C_2$ (kPa-s) |
| 1% 110mT | 2.0837 | 57.7647 | 9.4899 | 19.8832 |
| 220mT | 3.7503 | 113.5787 | 11.0573 | 38.2406 |
Chapter 3: Viscoelastic Behaviors of MRSTF

<table>
<thead>
<tr>
<th>Magnetic Field [mT]</th>
<th>Parameter 1</th>
<th>Parameter 2</th>
<th>Parameter 3</th>
<th>Parameter 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>110 mT</td>
<td>2.0</td>
<td>2.5</td>
<td>3.0</td>
<td>3.5</td>
</tr>
<tr>
<td>220 mT</td>
<td>3.0</td>
<td>3.5</td>
<td>4.0</td>
<td>4.5</td>
</tr>
<tr>
<td>330 mT</td>
<td>4.0</td>
<td>4.5</td>
<td>5.0</td>
<td>5.5</td>
</tr>
<tr>
<td>440 mT</td>
<td>5.0</td>
<td>5.5</td>
<td>6.0</td>
<td>6.5</td>
</tr>
</tbody>
</table>

![Graphs](image1.png)

**Figure 3.15.** Parameters variation with respect to external magnetic field

**Figure 3.16.** A comparison between experimental data and model-predicted results with the input strain amplitude being 1%
3.4 Conclusion

In this chapter, the rheological test of both steady shear and dynamic oscillatory tests featuring strain amplitude variation and frequency changes are applied to the MRSTF sample under different levels of external magnetic fields. The LVE and NLVE response for system are defined and analyzed.

It is found that in this dynamic experimental setting, the strain amplitude should be considered as the factors that bring about non-linearity to the target viscoelastic material as well as their mechanical behavior. The external magnetic field is the factor changing the system stiffness rather than non-linearity.

From the oscillatory experimental setting applied in this work, the fabricated mixture system of MRSTF exhibited strain and frequency dependence that is quite assemble to MRF, which indicates that the MR effect has a dominant role when iron particles are introduced to STFs under dynamic excitation where actual shear rate in dynamic oscillatory test might not be sufficient to trigger shear thickening effect.

A four-parameter viscoelastic model was used to describe the performance of MRSTF. It is clearly demonstrated that the parameters of the four-parameter viscoelastic model that were identified possessed a tendency to increase with the magnetic field. The comparison between the experimental results and the model-predicting values demonstrates that the model could represent the MRSTF performance effectively.
Chapter 4 Stress Relaxation of MRSTF

4.1 Introduction

Beside the dynamic mechanical analysis (DMA) featuring steady and dynamic shearing tests conducted in previous chapter, stress relaxation experiment is also considered a useful method towards the understanding of the viscoelastic properties. In this chapter, the experimental study and analysis of the stress relaxation behavior of MRSTF will be presented under various step strains. The experiments are conducted by an advanced rheometer with parallel-plate configuration with the function of strain control. The applied strains are in a wide range from 0.05% to 100%, which reveal a comprehensive information of MRSTF in both pre- and post-yield regions.

4.2 Experimental setup

The MRSTF sample is fabricated with the same fraction as indicated in previous chapter. The step relaxation experiment is conducted using the stress/strain-controlled rheometer adopting parallel-plate configuration. The diameter of the upper plate is 20 mm and the gap between the two plates is 1.0 mm. Before each test run of the the relaxation experiment, the MRSTF sample would experience an initial shear at $\dot{\gamma} = 10$ s$^{-1}$ for 2 minutes, and then the magnetic field is applied for 2 minutes to fully activate the material.

The schematic of the stress relaxation test is explained in Figure 4.1:

An instantaneous step strain $\gamma_0$ is applied at time $t=0$, and is maintained for the time period of the test run (Figure 4.1 (a)). Then, starting from $t=0$, the time dependent relaxation stress $\tau(t, \gamma)$ is recorded over the period of experiments (Figure 4.1 (b)).

The stress relaxation modulus, $G(t, \gamma)$, (Figure 4.1 (c)), may be achieved as the ratio of relaxation stress to the applied strain level, as given in Equation 4.1.
\[ G(t, \gamma) = \frac{\tau(t, \gamma)}{\gamma_0} \quad 4.1 \]

Figure 4.1 Schematic of stress relaxation with simple step strain method: (a) Applied step strain; (b) time-dependent relaxation stress; (c) calculated stress relaxation Modulus

The basic mechanism of stress relaxation is viscous flow [173]. In amorphous viscoelastic materials, the stress is relaxed by molecules sliding past each other reducing applied internal forces over an extended period of time. In solids, the relaxation time can be infinite and \[ G(t, \gamma) \] approaches a constant finite value \[ G_\infty \] [178].

### 4.3 Experimental results

The stress relaxation tests are carried out under the strain-controlled mode. The applied strain varies from 0.05% to 100%, covering both the pre-yield and post-yield regions at room temperature. The stress relaxation modulus, \[ G(t, \gamma) \] is recorded, the
influence of magnetic field flux density \(B\) and constant strain level \(\gamma_0\) over this relaxation modulus is both investigated.

4.3.1 Strain dependence

The time dependence of the stress relaxation modulus \(G(t, \gamma)\) under various amount of strain deformation is presented in Figure 4.2, at a constant magnetic field of \(B=220\text{mT}\) (a) and 330mT (b). It can be seen from the figure that the stress relaxation modulus \(G(t, \gamma)\) follows a descending trend before approaching a constant plateau value \(G_P\). The constant plateau value with respect to step strain \(G_P(\gamma)\) for the stress relaxation test conducted at \(B=220\text{mT}\) can be summarized in Figure 4.3. Observing the figure, when the step strain is small and within the LVE range, the plateau value \(G_P\) is almost independent to the level of strain and MRSTF may be considered perfect solid. As the step strain begins to increase, a dramatic decrease of \(G_P\) could be observed.

The decrease can be explained in following way:

The morphology of the MRSTF under certain level of magnetic field is the chain-like alignment in accordance to the magnetic flux density, and the silica particles in this system take certain equilibrium orientation as they are not affected by external field. Then transient load of deformation is applied to the balanced structure, the microstructure would rearrange upon the perturbation and the effect of magnetic field towards new equilibrium. If the strain is small, for instance lower than 0.1% within LVE range, the iron particle chain is not destroyed, and then due to the internal elasticity of the iron particle chain, the chain-like structure could be maintained. At large strains beyond LVE range of about 0.5%, the chain is deformed and the particle distribution is more oriented according to the direction of strain amplitude applied, which leads to smaller relaxation modulus. As the strain is getting even larger, the alignments within the fluid system are destroyed further or even completely ruptured, thus the experimental relaxation modulus takes even smaller value. The shape of
$G(t, \gamma)$ curves with different strain amplitudes reflect an image of the recovery process upon transient loading with/without break-up process.

It is also worth to point out that Figure 4.3 is in good accordance to Figure 3.4 in defining the LVE and NLVE transition, which demonstrates the dynamic properties of MRSTF samples. This result indicates that the stress relaxation experiment is also a feasible method in investigating viscoelastic materials.

Figure 4.2 Relaxation test result of MRSTF under various strain levels, B=220mT
Figure 4.3 Constant plateau of stress relaxation modulus with respect to step strain level, B=220mT

4.3.2 Field strength dependence

Figure 4.4 shows the stress relaxation modulus of MRSTF $G(t, \gamma)$ at various magnetic flux densities under a step strain of 0.05%, which is within the LVE range. It is seen from the figure that the relaxation modulus increases with the increasing field strength. Figure 4.5 summarizes their respective plateau values with the change of applied intensity.

Figure 4.4 Stress relaxation modulus $G(t, \gamma)$ under a small step strain of $\gamma_0 = 0.05\%$ upon various magnetic field flux densities, B=110, 220, 330, 440mT
Figure 4.5 Plateau value of stress relaxation modulus with respect to field strength,
\[ \gamma_0 = 0.05\% \]

Figure 4.6 demonstrates the stress relaxation modulus \( G(t, \gamma) \) at various field strength under the strain of 100\%, which lies in NLVE range. It can be seen that the plateau values of stress relaxation modulus in this case exhibit similar field dependence behaviour to the case when \( \gamma_0 = 0.05\% \), despite the actual values are of about three orders smaller comparing to the small strain situation.

Figure 4.6 Stress relaxation modulus \( G(t, \gamma) \) under a large step strain of \( \gamma_0 = 100\% \) upon various magnetic field flux densities, \( B = 110, 220, 330, 440\, \text{mT} \)
4.4 Modelling approach

The stress relaxation $G(t, \gamma)$ obeys the principle of time-strain separability, which means the relaxation modulus can be factorized into the products of two functions:

$$G(t, \gamma) = G(t)h(\gamma) \tag{4.1}$$

where $G(t)$ is known as linear relaxation modulus, which is only time dependent without changing with strain difference and $h(\gamma)$ is a strain dependent damping function that inversely related to strain deformation, and approaches unity. $h(\gamma)$ determines non-linearity of the step strain response of MRSTF.

Historically, several forms of damping function have been proposed to capture the viscoelastic properties of the materials. Wagner proposed a simple form of single exponential function [179], as given in Equation 4.2:

$$h(\gamma) = \exp(-a \gamma) \tag{4.2}$$

However, this damping function could not describe large strain. Thus Osaki [180] proposed a sum of two exponential functions, as given in Equation 4.3:

$$h(\gamma) = f \exp(-n_1 \gamma) + (1 - f) \exp(-n_2 \gamma) \tag{4.3}$$

This two exponential function form fit the large strain well, but is unable to predict at the small strain region where data approach unity in a sigmoidal manner. Thus Papanastasiou [181] proposed damping function in sigmoidal form, as described in Equation 4.4

$$h(\gamma) = 1/(1 + a\gamma^2) \tag{4.4}$$

However, the choice of $\gamma^2$ in denominator makes the damping function over predicted at low strains and unpredicted at high strains. The most used form of damping function is proposed by Soskey and Winter [182] by introducing another parameter as the order of denominator, which is sigmoidal in nature and predict the data well over the entire strain region:

$$h(\gamma) = 1/(1 + a\gamma b) \tag{4.5}$$
The linear stress relaxation modulus, \( G(t) \) usually takes the form of exponential series:

\[
G(t) = G_0 + \sum_{k=1}^{m} G_k e^{-t/\tau_k}
\]

Where \( G_i \) and \( \tau_i \) are the modulus and the relaxation time-constant of the \( i \)th mode, both being function of material properties.

For simplicity, Equation is usually reduced to a three parameter form, as given in Equation 4.7:

\[
G(t) = G_0 + G_1 e^{-t/\tau}
\]

Thus, by fitting the three parameters \( G_0, G_1, \) and \( \tau \), we are able to generate a master curve of \( G(t) \) for all the stress relaxation curves of various strain deformation under same experimental setup, as \( G(t) \) is an intrinsic value and does not evolve with the change of strain deformation. The parallel curves in Figure 4.2 prove this argument. Then the damping function may be determined according to the strain variation, so as to numerically duplicate the stress relaxation behavior of MRSTF samples.

As is given in Figure 4.7, the master curves of linear stress relaxation modulus of MRSTF samples at different magnetic field flux densities are fitted by the three parameter function with acceptable accuracy. The resultant identified parameters possess certain trend can also be summarized in the following Table 4.1, which are field dependent as also illustrated in Figure 4.8.

### Table 4.1 Resultant fitting parameters of \( G(t) \) for MRSTF samples at different magnetic field flux densities

<table>
<thead>
<tr>
<th>B (mT)</th>
<th>110mT</th>
<th>220mT</th>
<th>330mT</th>
<th>440mT</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G_0 ) (Pa)</td>
<td>13600</td>
<td>33600</td>
<td>48900</td>
<td>78000</td>
</tr>
<tr>
<td>( G_1 ) (Pa)</td>
<td>4200</td>
<td>5000</td>
<td>20100</td>
<td>25000</td>
</tr>
<tr>
<td>( \tau ) (s)</td>
<td>20</td>
<td>28</td>
<td>42</td>
<td>78</td>
</tr>
</tbody>
</table>
Figure 4.7 The fitting of master curves of $G(t)$ for MRSTF samples at different magnetic field flux densities

Figure 4.8 Fitting parameters for $G(t)$ with respect to magnetic field flux densities

Then, taking the example of $B=330\text{mT}$, $h(\gamma)$ is identified and multiplied to the
resultant master curves in different field strengths to rebuild the actual experimental curve. We first determine the ratio between the stress relaxation modulus curve and the master curve occurred in small step strain as given in Table 4.2.

**Table 4.2** \( h(\gamma) \) values at varied strain steps

<table>
<thead>
<tr>
<th>( \gamma )</th>
<th>0.5%</th>
<th>1%</th>
<th>5%</th>
<th>10%</th>
<th>50%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.71268</td>
<td>0.47916</td>
<td>0.1271</td>
<td>0.08846</td>
<td>0.02424</td>
<td>0.01213</td>
<td></td>
</tr>
</tbody>
</table>

Then parameter a and b can be determined with the form in Equation 4.5.

Then the parameters are determined:

\[
a = 214.9 \\
b = 1.167
\]

Finally, based on the parameters identified, the relaxation modulus can be reconstructed as given in Figure 4.9. And the degradation trend for damping function \( h(\gamma) \) is given in Figure 4.10.

![Figure 4.9 Numerically reconstructed stress relaxation modulus and actual experimental fact](image-url)
4.5 Conclusion

In this chapter, the stress relaxation of MRSTF under step shear strain is investigated experimentally as a feasible method of exploring viscoelastic properties of the materials other than dynamic mechanical analysis (DMA). The applied step strain ranges from 0.05% to 100%, and the stress relaxation modulus $G(t)$ is recorded exhibiting a constant value $G_P$, indicating elastic properties of MRSTF under field condition. A modelling approach is also applied to reconstruct the experimental data. This model consists of time-dependent of $G(t)$ and a strain-dependent damping function $h(\gamma)$. It has been shown that the model could accurately describe the stress relaxation modulus of MRSTF.
Chapter 5 Creep and Recovery Behavior of MRSTF

5.1 Introduction

In previous chapters, it is revealed that both dynamic mechanical analysis (DMA) and stress relaxation experiment are potent tools in investigating materials’ viscoelastic properties. Beside working in dynamic mode, liquid materials operate also in transient modes. Thus, designing novel liquids and devices requires knowledge on their response under transient conditions. Creep and recovery test is a method exploring materials’ properties at zero-to-low-flow rate. Moreover, the creep and recovery behavior of liquid materials are linked to microstructure variation in many ways.

In this chapter, the creep and recovery behavior of MRSTF under various constant shear stresses are investigated. The viscoelastic properties of MRSTF at various stress levels are revealed and analysed. Furthermore, the dynamic structure dependence of nonlinear viscoelastic properties is also discussed.

5.2 Creep and recovery behaviour of viscoelastic materials

Creep behaviour is defined as evolution of time dependent strain of viscoelastic material upon application of constant stress. When this constant stress is removed, the deformation will partially recover with the elapse of time, which process is referred to as recovery behavior. Rich rheological information about microstructure formation and convolution can be deduced from the both creep and recovery phases.

5.2.1 Creep phase

The schematic of creep and recovery of linear viscoelastic materials is presented in Figure 5.1. As it is shown in Figure 5.1 (a), a constant stress $\tau_0$ is instantaneously applied to sample materials at the beginning of the test, and it is maintained at equal level for a specific period $t_0$. The corresponding creep strain (Figure 5.1 (b)) with
respect to time elapse $\gamma_c$ can be expressed as given in Equation 5.1:

$$\gamma(t) = \gamma_s + \gamma_d(t) + \gamma_v(t)$$  \hspace{1cm} 5.1

where $\gamma_s$ is the instantaneous strain, the nonlinear time dependent component $\gamma_d(t)$ is called retardation strain, and $\gamma_v(t)$ is referred to as viscous flow.

For linear viscoelastic materials, the instantaneous strain $\gamma_s$ reflects elastic properties of the material. It is reversible and recovers immediately on the removal of constant stress.

Retardation strain $\gamma_d(t)$ is also referred to as delayed elastic strain, which recovers completely after certain period of time at decreasing rate. This unique character is attributed to the chain uncoiling [183].

The viscous flow $\gamma_v(t)$ is irreversible component of strain. It increases linearly with time for linear viscoelastic fluids.

Combining with Eq.1, burger’s model [184], as shown in Equation 5.2, is usually used.
applied to describe the experimental data of creep curves with fitting parameters determining the component of creep strain, thus providing helpful analysis to the deformation mechanism of the viscoelastic materials.

\[ \gamma_C(t) = \tau_0 \left[ \frac{1}{G_M} + \frac{1}{\eta_M} \left( 1 - e^{-G_K t / \eta_K} \right) + \frac{t}{\eta_M} \right] = J_C(t) \cdot \tau_0 \quad 5.2 \]

where \( t \) and \( \tau_0 \) refer to time elapse and constant stress respectively. \( G_M, \eta_M, G_K \) and \( \eta_K \) are separately the modulus of Maxwell spring, the viscosity of Maxwell dashpot, the modulus of Kelvin spring and the viscosity of Kelvin dashpot. \( J(t) \) defined as the ratio of creep strain and constant stress level, is called creep compliance (Equation 5.3).

\[ J_C(t) = \frac{\gamma_C(t)}{\tau_0} = J_e + J_d(t) + J_v(t) \quad 5.3 \]

### 5.2.2 Recovery phase

The recovery behavior of linear viscoelastic material after stress was removed at \( t_0 \), as illustrated in Figure 5.1(b), exhibited affined feature comparing to creep phase. Instantaneous elastic strain \( \gamma_e \) recovers immediately at \( t_0 \), retardation strain \( \gamma_d(t) \) recovers gradually with time elapse until a plateau is reached, which possesses an unrecovered deformation equal to viscous flow component \( \gamma_v(t) \). Hence, the time dependence of recoverable strain \( \gamma_R(t) \) is expressed in Equation 5.4:

\[ \gamma_R(t) = \gamma_e + \gamma_d(t) \quad 5.4 \]

Similarly, a recovery compliance function \( J_R(t) \) is given in Equation 5.5

\[ J_R(t) = \frac{\gamma_R(t)}{\tau_0} = J_e + J_d(t) \quad 5.5 \]

Thus, for linear viscoelastic behavior, the total creep strain \( \gamma(t) \) at any instant of time \( t > t_0 \) is superposition of two individual strains:

\[ \gamma(t) = \tau_0 J_C(t_0) - \tau_0 J_R(t - t_0) \quad (t > t_0) \quad 5.6 \]

where \( \gamma_C = \tau_0 J_C(t) \) represents the creep strain at \( t = t_0 \), and \( \gamma_R = \tau_0 J_R(t - t_0) \) corresponds to unloading at \( t = t_0 \).
5.2.3 Creep and recovery behavior of nonlinear viscoelastic materials

For most real materials, the time dependent mechanical behavior would be more complex. Especially for the nonlinear viscoelastic-plastic materials, the instantaneous creep strain may consist of both elastic component, as described in previous section, and plastic component. The plastic deformation is also unrecoverable during recovery phase, and it would be included in the residual strain and could be estimated by subtracting the viscous flow component from the residual strain. The details are presented in Figure 5.2 and Equation 5.7.

\[
\gamma_s = \gamma_e + \gamma_p \\
\gamma_r = \gamma_e
\]

5.3 Experimental setup

The MRSTF sample investigated in this creep and recovery assessment is 10\% wt of 5 \( \mu \text{m} \) carbonyl iron particles (C3518, Sigma-Aldrich) in a base medium of 25\% wt STF, which is a mixture of 14nm fume silica (S5505, Sigma-Aldrich) and ethylene glycol (102466, ReagentPlus, Sigma-Aldrich).

Dynamic yield stress (\( \tau_{dy} \)) is an important intrinsic parameter for viscoelastic liquids and a factor affecting the creep and recovery behavior of viscoelastic liquids. In order
to estimate $\tau_{dy}$ of MRSTF samples, a steady shear test is firstly applied to the 10% wt MRSTF samples. The test schematic starts with a slow constant shear rate of 10 s$^{-1}$ for 60 seconds to erase previous shearing history of the materials, and then it is followed by linear shear rate sweep from 0-100 s$^{-1}$. Another static procedure is placed in between the two steps for 100 seconds when external magnetic field is applied to the MRSTF samples at different flux densities. Shear stress values are recorded during the shear rate sweep progress. Following the steady shear test, the creep and recovery behavior is also examined through an advanced stress controlled rheometer with parallel-plate configuration, where the liquid sample of MRSTF is filled in the 1mm gap between 20mm diameter testing plate and material holder plate. Before commencing the experiment, MRSTF sample is subjected to a pre-experimental steady shear at 10 s$^{-1}$ for two minutes and magnetized in a quiescent state for another two minutes. A constant step stress is then applied to the MRSTF sample for 100 seconds and suddenly removed. The time history of the corresponding strain of the MRSTF sample is recorded at different field strength. Through the knowledge of dynamic yield stress $\tau_{dy}$ of MRSTF, the creep and recovery test is conducted with different step stress value below and beyond the threshold value of $\tau_{dy}$.

5.4 Experimental results

5.4.1 Yield stress of MRSTF

The shear stress vs shear rate curves for MRSTF are given in Figure 5.3. The field-off condition is presented in Figure 5.3 (a), where MRSTF possesses low shear stress at the beginning of the shear (as shown in inset figure) and increases dramatically after a critical shear rate is reached indicating shear thickening behavior. The field-on condition is shown in Figure 5.3 (b), where external magnetic field of B=198mT and 396mT is applied to MRSTF, respectively. MRSTF is found to exhibit mainly
magnetorheological behavior with well reduced shear thickening phenomenon upon the external magnetic field, as a conformed result to previous chapters. Then, \( \tau_{dy} \) could be estimated by directly extrapolating shear stress curve with respect to zero shear rate. Besides, the Herschel-Bulkley model taking the form of Equation 5.8 is also used to obtain the dynamic yield stress. The extent of model fitting for field-on condition is presented in Figure 5.4. And the \( \tau_{dy} \) is presented in Table 5.1.

\[
\dot{\gamma} = 0, \quad |\tau| \leq \tau_{dy}
\]
\[
\tau = \tau_{yd} \text{sign}(\dot{\gamma}) + K\dot{\gamma}^n, \quad |\tau| \geq \tau_{dy}
\]

5.8

Table 5.1 \( \tau_{dy} \) of MRSTF under different magnetic field

<table>
<thead>
<tr>
<th></th>
<th>0mT</th>
<th>198mT</th>
<th>396mT</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau_{dy} ) of MRSTF</td>
<td>0.5 Pa</td>
<td>680 Pa</td>
<td>900 Pa</td>
</tr>
</tbody>
</table>

(a)
Figure 5.3 Shear stress as function of shear rate for MRSTF under (a) field-off and (b) field-on condition

![Graph showing shear stress as function of shear rate for MRSTF under field-off and field-on conditions.]

Figure 5.4 Fitting of actual shear stress curves based on Herschel-Bulkley model

5.4.2 Creep and recovery behavior of MRSTF under various stresses

Applied constant stress level is an important factor affecting the creep and recovery behaviors for viscoelastic liquids. Series of creep and recovery experiments are launched to MRSTF samples without the application of magnetic field as illustrated in Figure 5.5. From Figure 5.5, it could be found that the strain response of MRSTF increased with the increase of shear stress applied. Besides, at absence of the external magnetic field, large strain deformation or slow flow may be triggered by even very small amount of shear stress. As could be seen from Figure 5.5 (b) and (c), the slope of response strain starts to show an increasing trend during the creep time when shear stress of just 1 Pa and 3 Pa is applied, indicating the liquid material is subject slow flow. This is due to the fact that when there was no magnetic field applied to the material, the iron particles were distributed randomly in the dispersion system, thus the mechanical properties of MRSTF would be dependent on carrier fluid, where the
dispersing iron particles are easily following the direction of shear stress. In this case, the creep and recovery behavior is invalid.

![Graphs showing creep and recovery behavior](image)

**Figure 5.5 Creep and recovery curves of MRSTF experiencing (a) 0.5 Pa, (b) 1 Pa, (c) 3 Pa, at absence of external magnetic field**

The creep and recovery behavior of MRSTF experiencing sequence of step stresses from 10 Pa to 1000 Pa at the magnetic field of 396 mT is presented.

\[ \tau_0 = 1 \text{ Pa} \]

Figure 5.6 shows the creep and recovery behavior for MRSTF at shear stress of 10 Pa. As can be seen from the figure, the creep strain is divided into three components: instantaneous strain, the retardation strain and the viscous strain. The instantaneous strain \( \gamma_s \) is equal to recovery strain \( \gamma_r \) that stages immediately after the removal of shear stress, indicating purely elastic nature. The retardation strain is gradually
recovered after shear stress is removed. The viscous component $\gamma_v$ is not recoverable. This phenomenon indicates that the MRSTF behaves as a linear viscoelastic material at this minimum shear stress of 10 Pa. The fact that the resultant instantaneous strain ($\gamma_s = \gamma_r = \gamma_e = 0.08\%$) is within LVE range of MRSTF demonstrates a conformed result of previous chapter and reflects how the creep recovery behavior is related to the viscoelasticity of liquid materials.

**Figure 5.6 Creep and recovery curve for MRSTF at small shear stress $\tau_0 = 10\text{ Pa}$, $B=396\text{ mT}$**

$\tau_0 = 5\text{ Pa}$

The creep and recovery curve for MRSTF at $\tau_0 = 5\text{ Pa}$ is presented in Figure 5.7.
In this case, the instantaneous strain is found to be slightly larger than the instantaneous recovery strain that reflects the elastic component of MRSTF behavior \((\gamma_s > \gamma_r)\). This is a clear evidence which indicates the involvement of plasticity strain component \((\gamma_p)\) in instantaneous strain \(\gamma_s\), which is also not recoverable like the viscous component \(\gamma_v\). Equation 5.9 demonstrates the contents of \(\gamma_s\) in this case.

\[
\gamma_s = \gamma_v + \gamma_p \tag{5.9}
\]

It is expected that the plasticity component increases gradually with the increase of the shear stress \(\tau_0\), as growing amount of shear stress would rapture the internal dipolar microstructure of MRSTF and lead to considerable resistance, like stretching and sliding, in structure reformation upon the stress removal [15, 185].

\(\tau_0 = 400 \text{ Pa}\)

The creep and recovery curve for MRSTF at \(\tau_0 = 400 \text{ Pa}\) is presented in Figure 5.8.
Observing this figure, it is found that the instantaneous strain increase with the increase of step shear stress. Besides, the proportion of plasticity strain component also increases with the increase of step shear stress.

$\tau_0 = 85 \text{ Pa}$

The creep and recovery curve for MRSTF at shear stress $\tau_0 = 85 \text{ Pa}$ is presented in Figure 5.9, which is approaching the dynamic yield stress of MRSTF.

$\tau_0 = 85 \text{ Pa}$
Observing this figure, beside the fact that the plasticity strain component continues to increase, the fraction of retardation strain component is nearly eliminated with the increase of step shear stress. Unlike the case of MRF [186], which behaves as a plastic solid and exhibits striking plastic tendency where, \( \gamma_e \ll \gamma_p \) or \( \gamma_r/\gamma_s \to 0 \), the MRSTF maintains fraction of elastic strain, which is immediately recovered after the shear stress is discontinued. This less pronounced plastic trend may be explained by the formation of the secondary microstructure of silica nano-particles clusters coexist with aligned carbonyl iron powders in MRSTF, especially upon the increase step shear stress. When the shear stress is removed, the clusters disassembles, thus the strain is recovered immediately. The entire suspension of MRSTF still behaves with combination of elasticity, plasticity and viscosity properties upon dynamic yield stress level as a result.

\[ \tau_0 = 1000 \text{ Pa} \]

When step shear stress is beyond dynamic yield stress, MRSTF sample starts to flow, as given in Figure 5.10.

![Figure 5.10 MRSTF tend to flow when shear stress is \( \tau_0 = 1000 \text{ Pa} \) exceeding dynamic yield stress, \( B=396 \text{ mT} \)](image)

To sum it up, MRSTF starts as elastic liquid when step shear stress is very small, as \( \gamma_r/\gamma_s \to 1 \). With the increase of shear stress, MRSTF’s behavior is approaching plastic solid, as the fraction of elastic strain is shrinking and the plastic strain is increasing. As the shear stress continues to increase towards yield stress, certain
fraction of elastic strain is maintained due to the viscoelastic properties of STF medium, MRSTF still behaves as solid with combination of elasticity, plasticity and viscosity properties. Until the step shear stress is beyond dynamic yield stress, MRSTF starts to flow as an elastic-plastic liquid. The ratio of $\gamma_r/\gamma_s$ is summarized in Figure 5.11 with the change of step shear stress.

![Figure 5.11 $\gamma_r/\gamma_s$ for MRSTF at different step shear stress, B= 396mT](image)

**5.4.3 Creep and recovery behavior of MRSTF under various magnetic field strength**

The most fascinating feature for MR material is magnetic controllability. The dependence of magnetic field on creep and recovery behavior of MRSTF constant stress of 100 Pa and 400Pa are presented in Figure 5.12 (a) and (b). From the figure, it could be found that the instantaneous creep strain showed a decreasing trend with increasing field strength for MRSTF. This result proved that the magnetic field could make MRF samples become stiffer from the perspective of time-dependent mechanical behaviors. Hence, the elastic modulus of rigidity ($G$), defined as the ratio of applied stress to the instantaneous creep strain ($G = \tau_0/\gamma_s$) also increased with the increase of external magnetic field.
5.4.4 Modelling approach

The creep strain could be numerically reconstructed by Equation 5.2, where \( t \) and \( \tau_0 \) refer to time elapse and constant stress respectively. \( G_M, \eta_M, G_K \) and \( \eta_K \) are separately the modulus of Maxwell spring, the viscosity of Maxwell dashpot, the modulus of Kelvin spring and the viscosity of Kelvin dashpot.

During parameter identification process, the time history of creep strain and constant step shear stress would be treated as input. Then, the four parameters \( G_M, \eta_M, G_K \) and \( \eta_K \) will be estimated based on non-linear least square method to minimized the error between the model-predicted creep strain and actual experimental facts.

The experimental results in Figure 5.12 are chosen to verify the optimization results. This optimization process is done by Matlab optimization toolbox. And the parameters are summarized in Table 5.2 and 5.3. The comparison between the numeric reconstructed results and experimental results are demonstrated in Figure 5.13.
Chapter 5 Creep and Recovery Behavior of MRSTF

Table 5.2 Estimated parameters for reconstruction of MRSTF creep strain, \( \tau_0 = 100 \text{Pa} \)

<table>
<thead>
<tr>
<th>Magnetic field</th>
<th>( G_K/\text{Pa} )</th>
<th>( \eta_K/\text{Pa} )</th>
<th>( \eta_M/\text{Pa} )</th>
<th>( G_M/\text{Pa} \cdot s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>198mT</td>
<td>10885</td>
<td>333.2676</td>
<td>131.5826</td>
<td>131.7934</td>
</tr>
<tr>
<td>396mT</td>
<td>22958</td>
<td>397.4396</td>
<td>264.4366</td>
<td>264.3535</td>
</tr>
</tbody>
</table>

Table 5.3 Estimated parameters for reconstruction of MRSTF creep strain, \( \tau_0 = 400 \text{Pa} \)

<table>
<thead>
<tr>
<th>Magnetic field</th>
<th>( G_K/\text{Pa} )</th>
<th>( \eta_K/\text{Pa} )</th>
<th>( \eta_M/\text{Pa} )</th>
<th>( G_M/\text{Pa} \cdot s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>198mT</td>
<td>1440</td>
<td>74.4309</td>
<td>15.4894</td>
<td>15.1007</td>
</tr>
<tr>
<td>396mT</td>
<td>6696.8</td>
<td>158.8731</td>
<td>32.4706</td>
<td>32.4721</td>
</tr>
</tbody>
</table>

Figure 5.13 Comparison of numerically reconstructed creep strain of MRSTF under different magnetic field flux densities (a) \( \tau_0 = 100 \text{Pa} \), (b) \( \tau_0 = 400 \text{Pa} \)

5.5 Conclusion

In this chapter, the experimental investigation of creep and recovery behavior of MRSTF samples is reported and numerically modelled. The effects of field strength and shear stress on the creep behavior are discussed. A four-parameter mechanical model is proposed to describe the creep behavior with proper accuracy.

The MRSTF is found to behave as a linear viscoelastic body at low step shear stress, and grow plasticity with the increase of the step shear stress. However, unlike the case
of MRF, which will gradually transform to pure plastic liquid upon the shear stress towards dynamic yield stress, the MRSTF sample maintains certain fraction of elasticity due to the formation of the secondary microstructures of silica clusters and exhibits combined properties of elasticity, plasticity and viscosity.
Chapter 6 A shear thickening liquid electrolyte based on ionic liquid

6.1 Introduction

Nowadays, the powerful energy storage devices based on highly conductive organic electrolyte have been prosperous and considered as an important power source for the sustainable development of human society that boost the industrial development significantly.

Nevertheless, the volatile and flammable nature of the organic electrolytes prove to be a major safety concern for further applications. In light of this, many efforts have been devoted to the design of anti-mechanical abuse package techniques which leads to innovative inventions that significantly improve the working stability of electronic devices upon disastrous scenario. However, the major concern over the organic liquid electrolyte is never dealt with. Consequently, in this research, we intend to develop a novel liquid electrolyte based on ionic liquids, which adopts the shear thickening phenomenon as intrinsic property of liquid electrolyte for better resistance on electronic devices against mechanical abuse.

As is revealed in this chapter, the experimental study and analysis of the proposed ionic liquid shear thickening fluid (ILSTF), including sample preparation, experimental setup and experimental results, are presented and discussed in detail. Besides, the mechanism related to the macro experimental facts is also substantially discussed.

6.2 Sample fabrication and experimental setup

6.2.1 Sample fabrication

Due to the well-established surface chemistry and the availability, nano-sized silica particle is used as dispersion phase in the proposed ionic liquid shear thickening fluid
Chapter 6 A shear thickening liquid electrolyte based on ionic liquid

(ILSTF). The specific silica particle chosen in our experimental study is Aerosil 200 from Evonik Degussa Corporation US. The Aerosil 200 is hydrophilic fumed silica with surface silanol (Si-OH) group and the primary particle size is 12nm in diameter. 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄, Sigma-Aldrich), which is one of the most studied ILs, is used as medium fluid. [BMIM]BF₄ possesses melting point of -71 °C and flashing point of 288 °C, thus a stable liquid during experiment investigation.

Prior to sample fabrication, the fume silica particles are heated at 110°C in a vacuum chamber for 24 hours, so as to eliminate water content attached to the surface of the nano-sized fumed silica particles. Then, the fumed silica particles are weighed and mixed with corresponding amount of [BMIM]BF₄ to a homogeneous state. After the mixture is substantially stirred, it is placed in vacuum chamber and dried for 6 hours under the temperature of 70°C, thus both air bubbles and moisture content are sufficiently removed prior to experiment investigation. 5 evenly dispersed ILSTF samples with varied fractions of silica particles 5%, 8%, 10%, 15% and 20%wt are fabricated.

6.2.2 Experimental setup

The rheological measurements are performed with the Anton Paar MCR301 rheometer. The rheometer adopts parallel plate configuration with the gap between the base plate and testing plate being 0.5mm. Also the thermal controller is applied to ensure the environment temperature of 20 °C in each test. The data is acquired and presented through built-in software rheoplus. Prior to each test run, a pre-shear at low shear rate of 10 s⁻¹ is conducted for 120 seconds, in order to cancel any previous shear history and to reinstate ILSTF samples’ equilibrium structures. Steady and oscillatory shear test are both conducted to the shear thickening liquid electrolyte samples.

Beside rheological test, a conductivity test is also conducted to examine the ILSTF samples’ conductivity variation under changing temperature for samples of different weight fractions. A heating coil is attached to the sample container, and the testing tip
is immersed into the liquid together with a thermometer to read the conductivity values at different temperatures.

6.3 Experiment scheme, result and discussion

6.3.1 Steady shear test

6.3.1.1 Scheme and results of steady shear test

As it is known, the shear thickening phenomenon is defined by rapid increase of shear viscosity upon the external loading of fast shear rate increase, thus rheological test under steady shear flow fits best in simulating the actual operating mode of the shear thickening fluid. Besides, the steady shear flow test is a most direct way to investigate the microstructural rearrangement by analysing the stress or shear viscosity response upon the variation of shear rate.

In order to investigate the shear viscosity response of the ILSTF and preliminarily confirm the existence of shear thickening phenomenon, the steady shear experiment is firstly adopted with the strain shear rate sweeping between the range of 0.1-1000 s⁻¹. The shear viscosity variation of all the samples at different fractions is presented in Figure 6.1. It is observed that the neat ionic liquid (indicated by the black line) exhibits nearly Newtonian behavior, as the values for the sample’s shear viscosity maintains at nearly a constant level of 0.34 Pa-s over the entire the sweep range.

As for the shear viscosity response of other ILSTF samples, several findings can be listed:

Firstly, samples of all fractions exhibit similar trend of shear viscosity changes over the testing range. When the shear rate is low, mild shear thinning behavior is observed, as the shear viscosity of all samples decreases slightly with the increase of shear strain rate. As the shear strain rate increases to a critical point, an abrupt increase with the shear viscosity are displayed by all the samples, which signals typical shear thickening performance. After that, a second shear thinning region can be traced at
even higher shear strain rate level for all the samples. 
Secondly, the onset of the shear thickening result is related to silica sample fraction. One can easily tell from Figure 6.1 that the critical shear rate point shifts left with the increase of silica sample fraction, which means earlier exhibition of shear thickening behavior. Moreover, the scale of peak shear viscosity value for higher fractioned sample is always significant higher than that of lower fractioned samples.

![Figure 6.1](image)

**Figure 6.1 Steady shear result for neat ionic liquid and shear thickening liquid electrolyte samples with silica fraction of 5%, 8%, 10%, 15% and 20%**

### 6.3.1.2 Mechanism of the shear thickening behavior

The observed shear thickening phenomenon is a direct reflection of internal mechanism of the sample transition, in this part we intend to theoretically explain the shear thickening behavior of the proposed ILSTF.

Modern SD simulation provided a fundamental explanation of the shear thickening mechanism, namely ‘hydroclusters’ [136] due to short-range lubrication forces acting between particles. Before the critical shear rate is reached for the sample, the shear thinning behavior of the liquid electrolyte samples may be explained as a consequence of microstructural rearrangement that reduces the resistance to flow. While as the shear rate is approaching critical point, shear thickening behavior is staged due to hydrodynamic interactions between dispersing colloidal particles. Then, upon the
relaxation of the sample flow, the clusters relax and the dispersion returns to equilibrium.

In the variation of shear rate from low shear to higher shear rate, the dispersing fumed silica nano-particles would be driven together and create a boundary layer in the colloidal dispersion of ILSTF. The probability for a particle to find neighboring particle is determined by the hydrodynamic lubrication force, which grows significantly during the course of shear strain rate increase, thus favors the formation of hydro-clusters in the liquid system. As a result, the microstructure and rheology changes fundamentally at the high shear rate, thus the transition from Brownian dominated regime to hydro-dynamics dominated regime which causes shear thickening. The evolution of the microstructures of the colloidal dispersion is shown in Figure 6.2. When shear strain rate is low, the colloidal interaction of the electrolyte dispersion is only related to the particle concentration, where higher fraction of fumed silica nano-particles would lead to increased steady-state shear viscosity, as shown in Figure 6.2 (a). As the shear strain rate increases, the original equilibrium structure of the dispersion is disrupted and follows the direction of shear loading, thus the dispersions exhibit shear thinning behavior due to the reduced particle interactions caused the fact that the dispersing silica particles adopts the direction of the flow of the shear loading, as pictured in Figure 6.2 (b). As the shear rate continues to increase, the hydrodynamic lubrication force between the dispersing fumed silica nano-particles begins to accumulate until it is sufficient to push the particles into close proximity, which makes the motion of the particles more and more correlated. Consequently, isolated silica nano-particles starts to form groups and chains, which eventually aggregates into hydro-clusters that provide dramatic resistance against the external shear loading and pronounced shear viscosity increase. This process is presented in Figure 6.2 (c). It is worthwhile to note that the so-called hydroclusters should not be considered aggregates or coalesced particles, but rather local transient fluctuations in particle density.
In Figure 6.1, a transition from shear thickening behavior to shear thinning behavior is also observed at high shear strain rate; this phenomenon marks an elasto-hydrodynamic limit of shear thickening and serves as a direct evidence that the colloidal particles themselves have a finite modulus. When the shear strain rate is high, particles are driven close to each other, and the shear stress gets higher as the trend continues. As the stress increases to a sufficiently high level, pair of particles in the suspension will elastically deform at close contact with a thin lubrication fluid layer in between, consequently, the cluster structure is disrupted to a certain level that causes a second shear thinning region at higher shear strain rate. This is known as an elastohydrodynamic deformation with hertzian contact [187].

6.3.2 Dynamic oscillatory shear test

The dynamic viscoelastic properties of ILSTF are investigated under following testing scheme

- Amplitude sweep mode: the driving frequency is set as a constant and the strain amplitude is swept from 1%-1000%, where the modulus variation can be determined on the sweeping range
• Frequency sweep mode: the strain is fixed at certain level and the frequency sweeps from low to high value of 1-628 rad/s, in this case the frequency dependence of ILSTF can be observed

6.3.2.1 Strain amplitude dependence

In this subsection, the strain amplitude dependence of the ILSTF is presented by varying the strain amplitude at different constant angular frequencies, and the nonlinear behavior of the samples at high strain deformation is summarised and explained.

Figure 6.3 gives the result for 20% ILSTF sample at 5 rad/s, from the figure we can see that the storage modulus is lower than loss modulus at around one order of magnitude over nearly the entire testing range, this behavior indicates that the ILSTF exhibits liquid like behavior. Moreover, with the strain amplitude reaching certain critical high level, both moduli display increasing trend with the increase of strain deformation. Theoretically, this kind of non-linear behavior is usually referred to as strain-hardening. It is considered that in case of strong interaction among the segments of complex fluids, like ILSTF discussed here, a composite microstructure is likely to be formed and resist flow alignment. And the behaviour of strain hardening exhibited by ILSTF is associated with this type of complex microstructure [59]. Indeed, strain-hardening is in a lot of occasions connected to strain-stiffening network components, or shear-induced network formation [188]. Besides, it is worth to point out that such behavior is fairly consistent with the reported dispersion of hydrophilic silica dispersion in PPG [110], which suggested similar shear thickening phenomenon occur in this IL based liquid system despite different solvent nature.

In other strain amplitude sweep tests, the same moduli variation is universally observed, which demonstrates obvious shear thickening phenomenon from dynamic point of view. Figure 6.4 is presented here to confirm the trend with the content of moduli comparison of lower fraction sample at the slight higher angular frequency.
Figure 6.3 Oscillatory strain sweep test (5rad/s) of 20% wt ILSTF

Figure 6.4 Oscillatory strain sweep test (10rad/s) of 8% wt ILSTF

Figure 6.5 gives the moduli variation for 15%wt ILSTF sample at varied angular frequency excitations. From the figure, we can see that the critical strain amplitude is getting smaller with increased angular frequency value. This result confirms that the shear thickening rheological behaviour of the ILSTF is relative both to the strain deformation and angular frequency level, as the dynamic shear rate is defined as the product of these two parameters.

In Figure 6.6, the loss modulus for pure ionic liquid is given, as the storage modulus is hard to obtain for this blank sample. Also observed from the figure, the loss modulus for the neat ionic liquid does not change in the entire experiment range, thus we can conclude that the neat ionic liquid behaves as a purely viscous Newtonian
fluid. Another evidence that support this conclusion is the experimental fact that the shear viscosity for ionic liquid remains stable in steady shear test, as presented in Figure 6.1.

![Figure 6.5](image1.jpg)

**Figure 6.5** (a) Strain swept storage modulus variation for 15% sample under different angular frequencies, (b) Strain swept loss modulus variation for 15% sample under different angular frequencies

![Figure 6.6](image2.jpg)

**Figure 6.6** Loss modulus for neat ionic liquid under varied angular frequency

From the complex viscosity point of view, which is considered dynamic equivalence of shear viscosity in steady shear experiments, the trend revealed in moduli comparison is substantially confirmed. Figure 6.7 gives the complex viscosity value for 10%wt ILSTF sample; we can see that the increased angular frequency results in more obvious shear thickening behavior and earlier critical strain amplitude point. The fraction dependence of complex viscosity for all the sample under the same angular frequency of 10rad/s is given in Figure 6.8; the result is that higher the
fraction of ILSTF would result in more obvious of shear thickening phenomenon for ILSTF samples.

![Graph of Complex Viscosity vs Strain for 10% ILSTF](image)

**Figure 6.7** Strain amplitude dependence of complex viscosity for 10%wt ILSTF sample at different angular frequencies

![Graph of Fraction Dependence of Complex Viscosity](image)

**Figure 6.8** Fraction dependence of complex viscosity vs strain amplitude for all samples (10 rad/s)

In summary, with the strain amplitude sweep test for different samples of ILSTF being displayed. We can come to a conclusion that the onset of dynamic shear thickening phenomenon is strictly related to angular frequency and sample fractions.
under this strain sweep setting. With higher the angular frequency and/or the sample fraction, more obvious shear thickening behavior is observed for the ILSTF.

What is also worth to note is the Newtonian behavior of neat ionic liquid obtained both in strain amplitude sweep test and steady shear flow test. This indicates that by adding dispersing colloids of fumed silica nano-particle, we have introduced not only shear thickening phenomenon to original ionic liquid system, but also distinct viscoelasticity to IL medium. This is significant, as this property can be, like shear thickening effect, granted many credits in safety issue for all the ionic liquid applications in case mechanical abuse. The reason is:

The elastic part of complex structure ($G'$) helps to spread the impact force on a bigger surface because of the immediate response of material. And the viscous part of the complex ($G''$) absorbs the impact by transforming into heat or molecular movement.

### 6.3.2.2 Angular frequency dependence

In this subsection, the angular frequency dependence of viscoelastic properties of ILSTF is presented. Also, the angular frequency dependence properties, which reveal the status of colloidal stability, will be discussed.

Figure 6.9 gives the moduli comparison of 15% wt sample in angular frequency sweep test with the strain deformation being 5%. Both storage modulus and loss modulus exhibit strong frequency-dependent behavior. Moreover, it is clearly seen that loss modulus is higher than storage modulus before approximately 10rad/s point which demonstrates that the system is characterized as a non-flocculated sol (liquid-like behavior), while storage modulus outweighs loss modulus beyond this point that indicates that the silica particles are colloidal unstable and flocculated into a three-dimensional particulate network in [BMIM]BF4 medium (solid-like behavior). Same character is also observed for other ILSTF samples tests as given in Figure 6.10 (concentrated sample with small strain amplitude) and Figure 6.11 (dilute sample with large strain amplitude).
Figure 6.9 Moduli comparison of 15% wt ILSTF sample in dynamic angular frequency sweep test (5% strain)

Figure 6.10 Moduli comparison of 20% wt ILSTF sample in dynamic angular frequency sweep test (1% strain)
Figure 6.11 Moduli comparison of 5% wt ILSTF sample in frequency sweep test

(20% strain)

Because colloidal stabilization based on electrostatic repulsion hardly occurs in ILs, as a consequence of high ionic strength of IL, even though the particles are assumed highly charged, thus the $[\text{BF}_4^-]$ anion-based ILSTF samples imply other repulsive interactions such as steric hindrance and a special solvation force. These two sources provide proper interface colloidal stability without requiring additional stabiliser.

For the steric hindrance:
IL molecules (ions) that attached to colloidal surfaces may be bulky enough to separate each colloidal surface. Or cations in ILs may be composed of both non-polar and polar groups, which can be adsorbed onto either hydrophilic or hydrophobic colloidal surfaces. Thus the steric stabilization would be optimized by the appropriate choice of ions of ILs and/or surface modification.

For repulsive solvation force:
It is considered a plausible explanation for the stability in the current ILSTF interface. The ILs are classified into a structure forming liquid by hydrogen bonding, cation-$\pi$ interaction, and intermolecular Van der Waals interaction between ions, which is able to introduce strong repulsive solvation force in the vicinity of IL-particle interface. In our case, $[\text{BF}_4^-]$ anions may interact with the hydrophilic silica particles through hydrogen bonding between the F atoms of $[\text{BF}_4^-]$ anions and the surface silanol groups, thus ensures the colloidal stability of the ILSTF samples.
From also the complex viscosity point of view, the strain deformation dependence of complex viscosity for 10% ILSTF sample is given in Figure 6.12 in the angular frequency sweep experiment. From the figure, we can observe that shear thickening phenomenon happens at similar critical angular frequencies without exhibiting obvious difference between different strain amplitudes.

Frequency sweep test of various sample fractions under the same strain deformation is also presented in Figure 6.13. From this figure, the shear thickening behavior for ILSTF samples exhibits similar trend as that is observed in strain amplitude sweep tests that is shown in Figure 6.8, which confirms that both strain amplitude and angular frequency are related to the dynamic rheological properties of ILSTF.

**Figure 6.12** Complex viscosity with respect of angular frequency under different strain amplitude for 10%wt ILSTF sample

**Figure 6.13** Fraction dependence of frequency swept complex viscosity under 10% strain amplitude
6.3.3 Conductivity test

From both steady and dynamic oscillatory shear test of ILSTF, we have concluded that both the shear thickening behavior and viscoelastic property are introduced to the original neat ionic liquid, it is an appealing improvement for the ionic liquid electrolyte in case of electrochemical applications from the point of view of mechanical properties, which allows robust resistance against impact or any other forms of mechanical abuses. Thus in conductivity test, we desire to examine how fumed silica nano-particles addition would affect the conductivity of the original neat ionic liquid.

The conductivity for all samples is tested in elevated temperature, as presented in Figure 6.14. From the neat ionic liquid sample to 10%wt fraction ILSTF sample, the conductivity increase with the increase of both temperature and silica fraction. As for 15% and 20% wt ILSTF samples, the conductivity also increases with temperature, as viscosity decreases with the increase of temperature. However, the overall curves for these high fractioned ILSTF samples are lower than other samples with lower fractions of silica addition. This is because the effect from the increase of viscosity due to particle addition that decreases the conductivity outweighs other positive effects which increase the conductivity. The result is quite acceptable, as the existence of silica particle provides satisfactory protection mechanism and at the same time makes the ionic liquid even more conductive under moderate weight fractions up to 10%.
Chapter 6 A shear thickening liquid electrolyte based on ionic liquid

Figure 6.14 Conductivity variation of all the samples at increasing temperature

6.4 Conclusion

In this chapter, both rheological and conductivity tests are conducted to the ionic liquid based shear thickening fluid (ILSTF). The mechanical behavior of the ILSTF upon external shear loading is characterised and summarised, as well as the conductivity performance being investigated. Appealing outcome has reached: The addition of fumed silica nanoparticles has introduced obvious shear thickening behaviour to the original Newtonian ionic liquid. Besides, the conductivity of the ILSTF dispersion exhibits increase to some extent. These findings prove that the proposed ILSTF may be considered as novel high performance liquid electrolyte possessing intrinsic self-protection mechanism, which opens a brand new avenue for the development of intelligent liquid electrolyte materials.
Chapter 7 Novel Reversible and Switchable Electrolytes Based on Magnetorheology

7.1 Introduction

The intrinsically safe cell design of high-energy battery has attracted huge scientific attention. Consequently, the endeavour of replacing volatile flammable organic liquid electrolytes with high performance solid electrolytes has led to a new prospective on batteries research. However, most solid/gel electrolytes are easily deformed; under extreme deformation, leakage and/or short-circuiting can occur, and the conductive ability of current solid/gel electrolytes is yet to be comparable to commercial liquid electrolytes. In light of this, we intend to report a novel magnetorheological electrolyte (MR electrolyte), which responds precisely to the changes of an external magnetic field in this chapter. The proposed MR electrolyte is expected to operate as liquid electrolyte with low shear viscosity during the absence of external magnetic field, while as solid electrolyte upon the convenient application of external magnetic field when resistance against impact or mechanical abuse is needed at working condition. As such, the state change from a liquid to solid state of this proposed MR electrolyte can be actively switchable in real time without reduction in conductivity. Thus, this work introduces a new class of magnetically sensitive solid electrolytes that can operate in dual modes with enhanced impact resistance and leakage prevention measure through reversible active switching of their mechanical properties.

As is presented in this chapter, a novel reversible solid electrolyte based on magnetorheology is reported, combining excellent conductivity and mechanical properties that are responsive to field changes. This novel magnetorheological electrolyte (MR electrolyte) is generated by dispersing magnetic nanoparticles in a highly conductive IL, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([EMI]TFSI, Sigma-Aldrich). Fumed silica nanoparticles are also used to stabilise the magnetic particles in the liquid system. The proposed MR electrolyte exhibits
field-dependent properties and excellent conductivity. The shear viscosity of the MR electrolyte could be controlled by varying the magnetic field intensity. The effect of the magnetic field on the conductivity of the MR electrolyte is also investigated. The conductivity remains unchanged during state changes, when the electrolyte forms a viscoelastic solid. The performance of supercapacitors using such an MR electrolyte is also tested under the influence of an external magnetic field as a solid evidence of the electrolyte performance.

7.2 Experimental setup and testing scheme

7.2.1 Synthesis of the core/shell magnetic particles

Magnetic properties and an absence of redox activity are essential requirements for the nanoparticles used to generate MR electrolytes. The dispersed magnetic particles applied in this experimental investigation of MR electrolyte are magnetic nanoparticles iron (II.III) oxide (Fe₃O₄) coated with a layer of silica. This layer improved dispersion stability [189] when the particles are added to the IL. The silica layer also insulated the redox activity of the iron-containing nanoparticles.

The silica-coated iron (II.III) oxide nanoparticles (Fe₃O₄) are prepared through the hydrolysis of tetraethyl orthosilicate (TEOS) in an alkaline environment. The chemicals used in this synthesis include magnetic nanoparticles with a unit size of 50–100 nm (Alfa Aesar, United Kingdom), TEOS, (98%, Sigma Aldrich, US), aqueous ammonia (25 wt%, Sigma Aldrich, US) and ethanol (100%, Sigma Aldrich, US). All reagents were used without follow-up processing or purification:

First, 1 g of Fe₃O₄ nanoparticles was dispersed in 16 mL of deionised water and 80 mL of ethanol in an ultrasonic water bath. Then, 12 mL of aqueous ammonia (25 wt%) was added to the dispersion, and the mixture was stirred vigorously at room temperature. Next, 1.8 mL of TEOS was added dropwise basis over a 24 h period while the solution was stirred continually to ensure the Fe₃O₄ nanoparticles were completely coated. After this hydrolysis reaction was completed, the core shells
Fe₃O₄@SiO₂ nanoparticles could be obtained with a magnet. The particles were washed several times in deionised water and then dried at 50°C.

As revealed by TEM images (Figure 7.1 (a) and (b)), the cubic magnetic nanoparticles are completely covered by a transparent layer of silica with a thickness of approximately 12–15 nm. The cores of the magnetic cubic particles are in the range of 50–200 nm. The results of the vibrating sample magnetometer (VSM) tests [190] for the original and coated magnetic nanoparticles are shown in Figure 7.1 (c), revealing a reduction of magnetisation due to the silica coating layer. Cyclic voltammetry carried out in aqueous electrolyte containing magnetic nanoparticles with and without a silica coating layer (Figure 7.1 (d)) showed that the coated magnetic nanoparticles are no longer electroactive.

After the coating process, Silica-coated magnetic nanoparticles retain their magnetic properties, as evidenced by the fact that they could be collected from an aqueous solution with a magnetic stick.

Figure 7.1 Properties of the core/shell magnetic nanoparticles (a), (b) TEM images
of particles and clusters. (c) Vibrating sample magnetometer (VSM) results of magnetic nanoparticles with and without silica coatings. (d) Cyclic voltammetry (CV) of a carbon electrode in a 0.1 M phosphate buffer solution with Fe3O4 or silica-coated Fe3O4 nanoparticles at a scan rate of 50 mV/s over the range from -1.0 V to 0.3 V.

7.2.2 Stability test

Observation of sedimentation
To characterise the sedimentation, the MR electrolyte suspensions are stored in test tubes for one week, and the heights of the sediment-supernatant interfaces are monitored and recorded. A higher solid phase indicated a more stable electrolyte

Redispersion experiment
A 50 s⁻¹ pre-shear is applied to the liquid sample for 2 min, followed by a standby time of 1 min. A constant shear stress of 20 Pa is then applied to the liquid sample, and the corresponding shear rate is recorded. Another 3 min pre-shear was then applied to ensure the particles’ complete redispersion. These steps are then repeated after 15 min, 30 min, 60 min and 24 h. The derived shear rates are recorded in a log ramp manner, with increasing intervals from 0.1 s to 10 s recorded logarithmically. The resultant shear rate values are then compared to determine the state of aggregation. The redispersion experiment and all other rheological experiments were carried out on an advanced stress controlled rheometer (Anton Paar MCR 301, Germany). The unified geometry applied in these rheological tests was a pair of parallel plates with a 0.3 mm gap. All experiments are carried out at 20°C.

7.2.3 Rheological test

Magnetic sweep experiment
A 50 s⁻¹ pre-shear is applied for 1 min, followed by a 1 min standby time. The linear ramp of a perpendicular external magnetic field ranging from 0 to 660 mT is then
applied with a constant shearing of 0.01 s\(^{-1}\), and the instantaneous shear viscosity is recorded.

**Steady shear rate sweep experiment**

The shear rate sweep experiments start with a 50 s\(^{-1}\) pre-shear for 1 min. During the standby minute where no shear loadings are applied, the specific magnetic strength is applied in the perpendicular direction to trigger the magnetorheological effect. A log ramp shear rate from 0.01 to 500 s\(^{-1}\) is then applied to the fluid, and the shear stress and shear viscosity are recorded.

**Dynamic oscillatory shear experiment**

Oscillatory dynamic tests begin with a 50 s\(^{-1}\) pre-shear for 1 min. Oscillatory shear loading is applied to the MR electrolyte samples with increasing peak strain from 0.01–1,000% with a specific external magnetic field in the perpendicular direction, and the angular frequency is a constant value of 5 rad/s.

### 7.2.4 Conductivity of MR electrolyte

**Impedance tests**

Impedance tests between two quadrilateral stainless steel electrodes are carried out to determine the conductivity of the MR electrolyte samples. A pair of permanent magnets is used to supply a magnetic field. A gauss meter is used to record the field strength at each test while the field strength is changed by adjusting the distance between the pair of magnets. A series of impedance tests are carried out on the electrolyte samples with 0.5, 0.8, 1.0 and 1.2 wt% silica nanoparticles. The conductivities under various field strengths can be calculated as shown:

\[
\alpha = \frac{A}{LR_c}
\]

where \(L\) is the gap between the electrodes, \(A\) is the conductive area, and \(R_c\) is the resistance value at the highest frequency in the impedance tests.

**Charge/discharge performance**

Charge/discharge performance are all conducted at a current density of 1 A/g. The charge-discharge curves of the supercapacitors composed of a pair of carbon electrodes and different MR electrolytes are collected under different external
magnetic fields.

7.3 Experimental results and discussion

7.3.1 Stability of the MR electrolyte

7.3.1.1 Stability test results

The motivation for using the silica-coated magnetic nanoparticles originates from the research of Guerrero et al. [191], who proposed that the change in surface chemistry induced by the coating process could significantly increase the stability of the dispersions formed in ILs [192]. In addition, small amounts of silica nanoparticles are also used to stabilise the silica-coated magnetic nanoparticles in the MR electrolyte samples. A 5% weight fraction of silica-coated magnetic nanoparticles is used in line with other studies [193], where it is found that the dispersions are stable for more than seven days, and the slight increase in shear viscosity indicates that the impact on ionic conductivity is minimal. The effect of adding bare silica nanoparticles to the electrolyte is investigated over the range of 0.5–1.2 wt%. The shear viscosity of the resultant samples increases with the increase in the fraction of silica nanoparticles. The ability to flow is substantially suppressed with the addition of 1.2 wt% silica nanoparticles.

Two separate experiments are designed to examine the stability of the MR electrolyte: a stationary observation of sedimentation and a redispersion experiment. The result of the sedimentation observation is shown in Figure 7.2, where the normalised height, which is defined as the ratio of the solid phase height recorded during the observation period to the original height, is presented. The samples with higher fractions of silica nanoparticles are more stable. The 1.2 wt% sample exhibits almost no supernatant after the entire week-long observation period, whereas the sample with 0.5 wt% silica forms a sediment within 3–4 h, with a final normalised height of approximately 33%. The normalised heights for the samples containing 0.8 and 1.0 wt% silica
nanoparticles are 85% and 95.4%, respectively. When the stable samples are inverted, they rapidly redisperses without any observable compact sedimentation at the bottom of the test tube. This result confirms that the MR electrolyte samples exhibit outstanding colloidal stability. This behaviour is an important result because stable IL-based MRFs has previously only been prepared using ILs that possess relatively high viscosities and low conductivities [193]. The sample containing 1.2 wt% silica becomes highly viscous and begins to show the properties of a weak gel. Stable MR electrolyte samples with 0.8 and 1.0 wt% silica nanoparticles are considered potentially more useful, as they would be expected to have greater viscosity changes after the application of an external magnetic field.

In the redispersion experiments, constant shear stress is applied for different durations to investigate the reversibility of the aggregates formed in the liquid system. If the process is reversible, the corresponding shear rates would be approximately the same; if the process is not reversible, the shear rates would be considerably smaller. Figure 7.3 (a)-(c) show the redispersion results obtained for MR electrolyte samples with 0.8, 1.0 and 1.2 wt% silica nanoparticles, respectively. The sample with 0.5 wt% silica nanoparticles is not tested because it is proved unstable based on the sedimentation observations. The shear rate of the MR electrolyte with 0.8 wt% silica nanoparticles decreases by nearly 100 s⁻¹ after a 24 h settling period. The shear rates are comparable to each other for the MR electrolyte with 1.0 wt% silica nanoparticles over the 24 h period. The shear rates attained for the MR electrolyte sample with 1.2 wt% silica nanoparticles are similar but considerably smaller than those observed for other samples. These results indicate that the sediments formed by the MR electrolyte sample with 0.8 wt% silica nanoparticles during test are difficult to redisperse. By contrast, the sediments formed in the MR electrolyte sample with 1.0 wt% silica nanoparticles are not compact, and simple agitation restored the electrolyte to its original state. A weak gel state is noted in the MR electrolyte with 1.2 wt% silica nanoparticles (Figure 7.3 (c)). The MR electrolyte sample with 1.0 wt% silica nanoparticles is the most appropriate liquid electrolyte possessing sound colloidal stability.
Figure 7.2 Normalised heights of the MR electrolytes vs. time.
7.3.1.2 Stabilizing mechanisms of MR electrolyte

Typically, colloidal particles in carrier media are stabilised through repulsion forces, i.e., electrostatic, steric and/or structural solvation [194,195]. If these forces are not comparable to the van der Waals attraction, the particles form aggregates and settle out of the carrier media. In oil-based MRFs, surface surfactant layer substances are often used to introduce electrostatic repulsion and steric repulsion between the dispersed particles [59]. These substances include, but are not limited to, oleic acid, citric acid, tetramethylammonium and polymeric monomers [193]. However, if ILs are used as carrier media, the highly concentrated ions normally suppress the electrostatic effects and steric hindrance becomes a major contribution to the repulsion between particles [196].

In our work, the sedimentation of a solid phase inside a fluid system depends largely on the difference in density and viscosity of the carrier fluid. Because the [EMI]TFSI used in this study had a constant viscosity of only 50 cP and its density (1.52 g/cm³) was considerably lower than that of the dispersed particles (5.1 g/cm³),
the combined force of steric repulsion or the formation of a solvation structural layer is not sufficient to stabilise the magnetic nanoparticles. Thus, another mechanism is needed to stabilise the silica-coated magnetic nanoparticles in the liquid system [197], which is the formation of silica-IL composites [198]. When colloidal particles are added to ILs, interesting phenomena, such as reinforcement, shear thinning, shear thickening, gelation and shear-induced sol-gel transition, can be triggered [198]. Increasing the weight fraction of silica particles in the IL-based system leads to interactions between the silica nanoparticles and ions, thus forming inter-connecting 3-D networks throughout the entire volume of the dispersion. When the amount of silica particles in the IL reach a critical fraction, the silica nanoparticles are no longer dispersed separately but form clusters instead, where a glass transition would occur to form a gelled material [197]. Consequently, this gelation effect, where dispersions evolve from liquid-like behaviour to solid-like behaviour (Fig. 2d), would result in a higher viscosity than that of the original IL. The increased viscosity would be a highly effective cushion to stabilise the silica-coated magnetic nanoparticles in this work.

7.3.2 Rheological behaviour of MR electrolyte

7.3.2.1 Experimental results

The MR electrolyte rheology is characterised via magnetic sweep, shear rate sweep and oscillatory dynamic experiments to determine whether the novel MR electrolyte is magnetically sensitive and to quantitatively establish the range of field-induced mechanical properties of the MR electrolyte. The MR electrolyte is shown to experience a dramatic increase in shear viscosity in Figure 7.4 as the external magnetic field increases in the magnetic sweep test. The viscosity of EMITFSI (see inset in Figure 7.4) is shown to be constant and unaffected by external magnetic fields. The pictures in Figure 7.4 show that an external magnetic field solidifies the original liquid MR electrolyte samples. This indicates that the MR electrolyte is functional
over a wide range of field strengths. The ratio of the initial shear viscosity to the highest shear viscosity upon the application of an external magnetic field is a common indicator of the sensitivity to a magnetic field. The least viscous MR electrolyte sample with 0.5 wt% silica nanoparticles has a considerably higher ratio than the most viscous sample, which contained 1.2 wt% silica nanoparticles. The specific values were 1,370, 458, 329, and 102 for MR electrolyte samples with 0.5, 0.8, 1.0 and 1.2 wt% silica nanoparticles, respectively. This dramatic increase in the shear viscosity of the MR electrolyte during the magnetic sweep test indicates how an external magnetic field could manipulate the mechanical properties and the phase of the MR electrolyte.

![Figure 7.4 Magnetic sweep tests of the MR electrolyte samples](image)

One of the most intriguing features of IL-based colloidal dispersion systems is that the addition of silica nanoparticles could introduce unique shear-dependent non-Newtonian behaviour to the existing Newtonian carrier fluid, which is why steady shear experiments are used to investigate the shear-induced behaviour of the fabricated MR electrolyte samples. EMITFSI possesses a fairly low constant viscosity of 50 cP over the entire range of shear rates, which is an indication of typical Newtonian behaviour. However, for the MR electrolyte, shear-thinning behaviour is observed under zero-field conditions (Figure 7.5). A minor increase in viscosity is also observed at a relatively high shear rate, indicative of secondary clustering due to the additional silica nanoparticles. This phenomenon is beneficial because it could be
configured to serve as a fail-safe mechanism to protect the MR electrolyte against disastrous scenarios. Furthermore, the exact shear viscosity of the MR electrolyte could be determined under varied shear rates, whereby the addition of larger amounts of silica nanoparticles resulted in a higher initial shear viscosity, in agreement with direct observations. Figure 7.6 shows the shear stress variations for the MR electrolyte samples with respect to shear rate, whereby the notable increase in shear stress at a relatively high shear rate agrees with the shear viscosity changes presented in Figure 7.5. Similar rheological behaviours occurred at higher shear viscosity values when an external magnetic field is applied to the MR electrolyte samples, as presented in Figure 7.7 and Figure 7.8.

![Figure 7.5 Shear rate sweep test results for the EMITFSI and MR electrolyte samples, B=0mT](image)

Figure 7.5 Shear rate sweep test results for the EMITFSI and MR electrolyte samples, B=0mT
Figure 7.6 Shear stress vs. shear rate curves for the MR electrolyte samples indicating a secondary silica structure at a high shear rate, B=0mT
Figure 7.7 Shear rate sweep experiment of MR electrolyte with (a) 0.5%, (b) 0.8%, (c) 1.0%, (d) 1.2% wt silica addition under varied field strength $B=132\text{mT, 264mT and 396mT}$.

Figure 7.8 Shear stress vs. Shear rate flow curve of MR electrolyte samples with (a) 0.5%, (b) 0.8%, (c) 1.0%, (d) 1.2% wt silica addition under varied field strength $B=132\text{mT, 264mT and 396mT}$.

Oscillatory dynamic experiments are performed to investigate the viscoelastic properties of the electrolyte samples; these experiments reflect the microstructures of the materials. Figure 7.9 shows the strain sweep dynamic test results. The storage modulus starts to decrease at a strain deformation of approximately 10% for all four samples, defining an intrinsic linear viscoelastic range of the MR electrolytes, where the samples are sheared without breakage of the internal microstructure. This range is substantially wider than that for typical MRFs, indicating the advantage of IL-silica composites. The loss modulus is larger than the storage modulus over the entire
deformation range for MR electrolyte samples containing silica nanoparticles (0.5, 0.8 and 1.0 wt%), which confirmed a liquid-like behaviour. The values of storage and loss moduli are similar for the MR electrolyte sample with 1.2 wt% silica nanoparticles, illustrating a solid-like behaviour. The dynamic results are consistent with the steady-state shear results, indicating that 1.2 wt% silica nanoparticles engendered a liquid-to-gel transition for the MR electrolyte. Upon application of an external magnetic field, the alignment of the magnetic nanoparticles resulted in solidification, and the storage modulus becomes significantly larger than the loss modulus. The modulus increased with increasing external field strength, which is demonstrated in Figure 7.10.

![Figure 7.9 Oscillatory dynamic experiment for MR electrolytes, where the linear viscoelastic range of the MR electrolytes can be clearly observed.](image)

![Figure 7.9 Oscillatory dynamic experiment for MR electrolytes, where the linear viscoelastic range of the MR electrolytes can be clearly observed.](image)
Figure 7.10 Shear strain sweep of oscillatory dynamic experiment of MR electrolyte samples with (a) 0.5%, (b) 0.8%, (c) 1.0%, (d) 1.2% wt silica addition under varied field strength \( B = 132 \text{mT}, 264 \text{mT} \) and \( 396 \text{mT} \)

7.3.2.2 Rheological mechanism of the MR electrolyte

Shear thinning is indicative of a disruption in the internal networks after external mechanical loading. This rheological characterisation reflects the evolution of the alignment of the silica-coated magnetic nanoparticles in the MR electrolyte samples when external shear loading is applied. The slight shear-thickening trend at higher shear rates indicates the secondary clustering structure of the inter-connecting silica-IL networks, which were used to stabilise the silica-coated magnetic nanoparticles in the electrolyte system. The liquid system reverts to its original state when the shear loading is removed. When external magnetic fields are applied to the MR electrolyte samples, similar rheological behaviour is observed at higher viscosities. The increasing shear viscosity is attributed to the orderly alignments of dispersed silica-coated magnetic nanoparticles in the presence of a magnetic field.
7.3.3 Conductive ability of the MR electrolyte

7.3.3.1 Experimental results

Impedance tests

The impedance tests, as introduced in previous section, are conducted to the MR electrolyte samples under different magnetic field to investigate the effect of magnetic field on the conductive ability of the proposed MR electrolyte. Figure 7.11 (a)-(h) present the Nyquist plots of the MR electrolyte samples derived from the impedance test. And Table 7.1 summarises the conductivity values of the MR electrolyte samples. Despite the electrolyte's increasing shear viscosity in response to increasing magnetic field strength, the conductivity of the MR electrolyte remains nearly constant (calculated conductivity results are also presented in Figure 7.12). The conductivity is only slightly lower than the neat IL electrolyte. This slight decrease is attributed to the addition of silica nanoparticles, which formed a 3-D network with the IL medium. The results indicate that an external magnetic field could be used to control the mechanical properties by manipulating the phase of the MR electrolyte samples from liquid to semi-solid without any negative effects on conductivity.
Figure 7.11 Nyquist plots of MR electrolytes under various external magnetic fields with (a) 0.5%, (c) 0.8%, (e) 1.0%, (g) 1.2 wt% silica nanoparticles and their related expanded view (b, d, f, h).
Figure 7.12 Conductivity result of neat [EMI]TFSI and MR electrolyte with varied silica addition under different field strength $B=0$, 120, 240, 360 mT

**Table 7.1 Summary of impedance test**

<table>
<thead>
<tr>
<th></th>
<th>0 mT</th>
<th>120 mT</th>
<th>240 mT</th>
<th>360 mT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_c$ (Ω)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$ (mS/cm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IL</td>
<td>141.3</td>
<td>5.83</td>
<td>141.4</td>
<td>5.83</td>
</tr>
<tr>
<td>MR electrolyte + 0.5% silica</td>
<td>146.4</td>
<td>5.69</td>
<td>146.9</td>
<td>5.67</td>
</tr>
<tr>
<td>MR electrolyte + 0.8% silica</td>
<td>153.5</td>
<td>5.44</td>
<td>157.2</td>
<td>5.32</td>
</tr>
<tr>
<td>MR electrolyte + 1.0% silica</td>
<td>162.0</td>
<td>5.13</td>
<td>160.8</td>
<td>5.17</td>
</tr>
<tr>
<td>MR electrolyte + 1.2% silica</td>
<td>174.7</td>
<td>4.72</td>
<td>174.9</td>
<td>4.71</td>
</tr>
</tbody>
</table>

Charge-discharge test

MR electrolyte samples are used to assemble supercapacitors. Charge/discharge performance comparisons of the supercapacitors using the MR electrolytes with 0.8, 1.0 and 1.2 wt% silica nanoparticles are presented in Figure 7.13 (a)-(c). No significant decrease in capacity was observed, even when the magnetic field is applied. This charge-discharge experiment should be considered direct evidence that an external magnetic field does not affect the operation of an electronic device that uses an MR electrolyte despite the change in the mechanical properties. The charge-discharge curves of the supercapacitors assembled with various electrolyte compositions under specific magnetic fields are shown in Figure 7.14 (a)-(c). A larger quantity of silica nanoparticles causes a decrease in overall performance, regardless of the external field strengths.
Figure 7.13 Charge-discharge curves of supercapacitors using MR electrolytes containing silica-coated magnetic nanoparticles at concentrations of (a) 0.8 wt%, (b) 1.0 wt%, and (c) 1.2 wt% under magnetic strengths B=0, 120 and 240 mT.
Figure 7.14 Charge-discharge behaviour comparison of the supercapacitors using different MR electrolytes samples at the same magnetic fields of (a) 0 mT, (b) 120 mT, and (c) 240 mT.

7.3.3.2 Proposed mechanism for conductivity of MR electrolyte

Ionic conductivity is determined by ionic mobility and carrier concentration [199]. In our conductivity tests, there were two components that could affect the transportation of ions (compared with the neat IL): the silica-IL interface and the alignment of silica-coated magnetic nanoparticles under an external magnetic field. The interconnecting silica-IL cluster would consume some ions, an equilibration occurring between the formation and destruction of the composite structure, which is why the MR electrolyte samples are less conductive when higher fractions of silica nanoparticles are added. In our study, the gelation effect introduced to maintain the stability of the electrolyte dispersion is kept at a minimum, so the sample remains liquid rather than transforming into a gel. Thus, the reduction of effective ionic carriers is minimised [194]. When no external magnetic field is applied to the MR electrolyte, the magnetic nanoparticles disperse randomly due to the combined effects of Brownian forces and the stabilising network interface between the silica particles and IL, and thus, the conductive elements that carry the charges flow smoothly throughout the liquid system.

When an external magnetic field is applied to the MR electrolyte in a direction
perpendicular to the testing cell, the field-induced magnetostatic force would result in
a bipolar effect that binds the sensitive magnetic nanoparticles into elongated
alignment [200]. This bipolar effect is achieved when magnetic nanoparticles are
placed in a uniform magnetic field, creating magnetic moments due to the
magnetisation of all particles. These magnetic moments lead to interactions between
adjacent particles on both sides of the particle, resulting in finite alignment lengths.
The transition leads to significant changes in rheology and phase of the MR
electrolyte, as shown in Figure 7.4. There could be a number of possible structures of
the field-induced aggregates, including spheroidal, cylindrical, and layered particle
aggregates or free single chain, columnar and other labyrinthine structures [200-202].
The particular structure formed depends on the initial volume fraction and the
parameter $\lambda$, i.e., the ratio of the magnetic field energy to the thermal force [200]. In
this study, considering the dilute concentration of magnetically sensitive nanoparticles
used and the effective steric repulsion force generated by the silica-IL composite
[196], the magnetically sensitive silica-coated magnetic nanoparticles would form a
stable chain-like or column-like structure along the direction of an applied magnetic
field. The orderly geometric structure in the dispersion system acts as a sponge, where
the remainder of the space is filled with IL. Because the unfilled space is considerably
larger than the ions, their mobility is not affected by the alignment of the magnetic
nanoparticles, which explains why the conductivity was not significantly affected
upon the application of magnetic fields. A schematic of the mechanism is presented in
Figure 7.15. This result explains why conductivity is not significantly changed and
sheds light on the optimisation of the microstructure of novel solid electrolytes based
on magnetorheology by introducing a permanent matrix. Because the transportation of
effective charge carriers is not affected by external magnetic fields applied to MR
electrolytes, the effect of temperature on an MR electrolyte would be the same as for
IL, where higher temperatures would accelerate the charge carrier motion, leading to
increased conductivity [203].
7.4 Conclusion

In this chapter, an MR electrolyte is fabricated based on IL and silica-coated magnetic nanoparticles. The MR electrolyte demonstrates low shear viscosity and prominent colloidal stability during the absence of external magnetic field, as evidenced by sedimentation and redispersion tests. The reversible significant increase in shear viscosity and even change of state could also be exhibited by the novel MR electrolyte upon the application of external magnetic field without observable reduction in conductivity, despite dramatic increases in the field-induced shear viscosity. These rheological and conductivity experiments prove that that the MR electrolyte samples exhibit a well-defined field-induced phase transition, which confirms the novel application of magnetorheology to electrolyte research. The significance of this unique property of the fabricated MR electrolyte is that the mechanical properties of the MR electrolyte in electrochemical devices could be controlled from liquid to solid without negatively affecting the conductivity. Thus, devices incorporating this novel electrolyte would possess an active controllable source for improved safety feature and operating stability.
Chapter 8 A novel class of ionogels with a controlling structure based on Magnetorheology

8.1 Introduction

Ionogels are a new class of hybrid materials where ionic liquids are immobilised on solid supports. Ionogels eliminate any concerns about the leakage of corrosive and toxic ionic liquid while maintaining their appreciable physiochemical properties. However, excessive amount of solid support matrix would sacrifice the conductivity of ionogel despite enhanced mechanical strength, which would trigger serious concerns over the manipulation of ionic liquids and solid components. Here, we report a novel elastomeric magneto-rheological ionogel (MR ionogel) by introducing structured magnetic nanoparticles into the scaffold of a UV cross-linked platform that possessed high ionic liquid fraction. The MR ionogels exhibits field responsive mechanical and conductive properties according to external magnetic field. The most important merits of the current MR ionogel is that the magnetic structures formed in the fabrication process, as revealed in previous chapter [41], should not hinder ionic motion but improve the mechanical strength of the resultant MR ionogel. Consequently, the introduction of magnetically sensitive components couldn’t cause any negative effects over the conductive performance of the MR ionogel. As a result, this work not only opens an avenue to synthesize robust ionogel possessing controllable physical properties for soft flexible electronic devices, but also a novel class of MR elastomers with desired conductivity exhibiting sound potential in sensors and actuators applications.

In the context of this chapter, rheological and conductivity tests as well as microscopic observations of the are carried out to characterize the physical properties of the proposed MR ionogel, and to investigate the effect of external magnetic field applied during material fabrication and in-use situation.
8.2 Fabrication of MR ionogel samples

The chemicals used in the fabrication of MR ionogel include PEGDA (Polyethylene (glycol) Diacrylate Mn=700 Sigma-Aldrich, US), HOMPP (2-Hydroxy-2-methylpropiophenone \(\geq 97\%\) Sigma-Aldrich, US), EMITFSI (1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide \(\geq 98\%\) HPLC Sigma-Aldrich, US) and PEO (Polyethylene Oxide Mv=4,000,000, powder Sigma-Aldrich, US). They are all used as received without further purification.

The magnetic nanoparticles are silica coated iron oxide nanoparticles, which are the same kind of particles used in Chapter 7 [41]. The magnetic properties and an absence of redox activity would ensure the magnetic nanoparticles being responsive to external magnetic field without concerning possible reaction with electrodes materials.

Three kinds of matrix ionogel precursors were generated and named as Ionogel A, B and C. Ionogel A is generated by mixing 8\%wt of PEGDA, 3\%wt of HOMPP with EMITFSI, and Ionogel B and C are fabricated with additional 1\%wt of PEO and 3\%wt of PEO, respectively. All the weight fractions are with respect to the weight of EMITFSI. Then the precursors are exposed to UV light source (6000mW/cm\(^2\)) for 10 minutes for the solidification. A photo of Ionogel A is shown in Figure 8.1.

The MR ionogel samples are generated by directly adding 10\%wt of silica coated iron oxide nanoparticles to ionogel A, B and C precursors to obtain MR ionogel A0, B0 and C0, and then the mixtures were cured under both a UV light source (6000mW/cm\(^2\)) and the magnetic fields of 60mT, 120mT and 240mT for an hour to obtain the samples of the MR ionogel A60, A120 and A240, MR ionogel B60, B120 and B240, MR ionogel C60, C120 and C240. A schematic of the fabrication process is shown in Figure 8.2.
8.2 Schematic of MR ionogel fabrication

The three kinds of matrix ionogel materials are fabricated with different amount of PEO addition in order to investigate how the field induced magnetic microstructure is established in the UV initiated ionogel matrix. The matrix ionogel samples are found to be softer and more flexible with growing amount of PEO addition. As will be revealed in following subsections, the properties of matrix material would exhibit some difference in the adoption of magnetic structure.

An exemplified MR ionogel sample is shown in Figure 8.3, which illustrates that MR ionogel possessed a freestanding status in a well-defined shape. A schematic of the composition of MR ionogel is also presented in Figure 8.4, which demonstrates that the field induced magnetic structure would transform from random distribution to an orderly alignment with the application of magnetic intensity.
8.3 Rheological experiment of MR ionogel

8.3.1 Experiment schemes

Both steady shear tests and dynamic oscillatory shear tests are conducted to the matrix ionogel samples and MR ionogel samples. The experiments are carried out by an advanced stress-controlled rheometer Anton Parr MCR 301 with a parallel plate configuration.

In steady shear experiments, the samples are cut into 20mm diameter discs and sheared between the tip of the testing plate and the sample holder plate. The sample remains static between the parallel plates and an external magnetic field of desired intensity is applied for 2 minute to ensure that the MR ionogel samples are fully activated by the external magnetic field. Then, a strain deformation is applied to the
samples and increases logarithmically over a wide range from 0.001% to 1000%; the magnetic field remains active during the shearing process, so as to record the corresponding shear stress value during the test.

In a dynamic oscillatory shear test, strain is applied in a sinusoidal wave with a sweeping strain amplitude. In this test the sample remains stationary while an external magnetic field of desired intensity is applied on for 2 minute to ensure the MR ionogel samples are fully activated, and then strain deformation is applied and increases logarithmically between 0.01% to 300% with a constant angular frequency value, the magnetic field remains active during the shearing process, and the dynamic parameters storage modulus (G’) and loss modulus G” are recorded. The dynamic oscillatory angular frequency sweep test is similar to a strain sweep test, except that the angular frequency varies logarithmically between 0.01-300 rad/s under a constant strain amplitude value.

No magnetic field is applied when testing ionogel matrix samples.

8.3.2 Rheological properties of ionogel matrix

Steady shear test

As shown in Figure 8.5, the shear stress of all three ionogel matrix samples increase almost linearly as the strain deformation increases until it reaches an intermediate strain level; which indicates the transition of pre-yield (linear range) and post-yield regions (non-linear range) of the ionogel matrix materials. Moreover, the initial shear stress decreases as more polymer is added, which is conformed to direct observation of ionogel samples where those with more PEO appears to be softer and more flexible.

The stress curves of all three ionogel matrix samples indicate certain differences despite overall similarity, the differences may be explained by the microstructure evolving with different amounts of PEO addition. The increased softness and flexibility of ionogel matrix samples with increasing amount of PEO addition is due to the inter-connecting polymer network being more prone to recoil upon the external
strain, thus some energy is absorbed during deformation and the response is more viscous than the immediate elastic response in shear stress. This growing fraction of polymer network may also explain the larger shear stress at the turning point of the pre-yield region and post-yield region shown in Figure 8.5, where more energy is needed to rupture the growing internal polymer network.

![Figure 8.5 Steady shear experiment of ionogel matrix samples](image)

**Dynamic oscillatory shear test**

The result of the dynamic oscillatory strain sweep test with a constant angular frequency of 5 rad/s for ionogel matrix samples is shown in Figure 8.6, and it reflects the viscoelastic properties of the ionogel matrix samples. Observing the figure, the storage modulus (G’) is generally larger than the loss modulus (G’’)) over a wide range of strain for all the ionogel matrix samples, thus exhibiting a rubbery behaviour. There is also a drop in G’ and a simultaneous increase in G’’ at higher strain deformations for all three samples, as highlighted by the parameters \(\gamma_{c1}\), \(\gamma_{c2}\), and \(\gamma_{c3}\). Moreover, when comparing the modulus value between samples, there is a slight decrease in G’ and an increase in G’’ as the fraction of polymer addition increases. The dynamic rheological behaviour of ionogel matrix samples may be explained in following paragraph:

The G’ plateau range shown in Figure 8.6 indicates the linear viscoelastic (LVE) range where the microstructures of viscoelastic materials are maintained despite the shear loading. The resultant drop in G’ and simultaneous increase in G’’ is due to a weaker
structural strength and increased energy dissipation associated to break-up of internal structure, when the samples are sheared beyond LVE, namely non-linear viscoelastic (NLVE) range. The parameters $\gamma_{c1}$, $\gamma_{c2}$ and $\gamma_{c3}$ that mark the LVE and NLVE transitional point for Ionogel A, B, and C values are coincident to the transitional point of pre-yield and post-yield region presented in Figure 8.5, where more polymer addition leads to an extension of LVE range. These results show that the addition of polymer favors the viscous component of the overall viscoelastic behaviour of the ionogel samples, and thus softer and more flexible materials.

An oscillatory angular frequency sweep test is carried out with a small strain of 1% and a relatively large strain of 10%, where the matrix ionogel samples operate in a separately linear viscoelastic (LVE) and non-linear viscoelastic (NLVE) range. Figure 8.7 gives the result of Ionogel A, B, and C tested with 1% strain, while the result for relatively large strain is shown in Figure 8.8. Both figures indicate that $G'$ and $G''$ followed an increasing trend as the angular frequency increased. The relative modulus values for all the ionogel samples decrease as the amount of polymer increases, which indicates once again that adding more polymer would lead to softer and more flexible materials.

Besides, the value difference between the $G'$ and $G''$ with 10% strain is smaller than that recorded with 1% strain for all the ionogel matrix samples, which agrees with the oscillatory strain sweep experiment where $G''$ approaches $G'$ in the NLVE range. Moreover, this specific value difference between $G'$ and $G''$ is also found to link with the amount of polymer addition when the samples are sheared in NLVE range. As is shown in Figure 8.8, the value difference in the modulus of ionogel C is larger than that of ionogel B and ionogel A in the NLVE range.
Figure 8.6 Dynamic oscillatory strain sweep experiment of ionogel matrix samples

Observing Figure 8.7 and Figure 8.8, the increasing trend of $G'$ and $G''$ with respect to angular frequency increases may be attributed to the relaxation of the PEO chain strands. Secondly, the reduced modulus value for the ionogel matrix at a large strain of 10% comparing to a smaller strain of 1% could be explained by the breaking up of the polymer network in NLVE range; which would result in a weaker structure and an increased dissipation of energy. Lastly, the fraction relevance of the specific value difference in modulus shown in Figure 8.8 indicates that the linear range extends from Ionogel A to Ionogel C, as the PEO polymer network grows and spread throughout the entire system. It is a solid evidence of how the structural variation could be deciphered by the overall mechanical properties.
Figure 8.7 Dynamic oscillatory angular frequency sweep experiment of ionogel matrix samples, $\gamma = 1\%$

Figure 8.8 Dynamic oscillatory angular frequency sweep experiment of ionogel matrix samples, $\gamma = 10\%$
8.3.3 Rheological properties of MR ionogel

The rheological behaviour of MR ionogel is investigated and summarised via the effect of the curing magnetic field and the MR effect of the MR ionogel samples exhibited upon an external magnetic field, respectively.

*The effect of the curing magnetic field*

Steady and oscillatory shear tests are carried out to examine how the curing magnetic field affected the rheological properties of the MR ionogel sample.

The results of a steady shear experiment of MR ionogel A, B, and C cured at different densities of magnetic flux are shown in Figure 8.9(a)-(c). The figures indicate that the shear stress curves of the MR ionogel samples increase as the curing magnetic field increases, until reaching a saturation at relatively higher curing magnetic fields, where the shear stress curves nearly overlap. Therefore, the curing magnetic field could be identified as a determiner of the mechanical properties of the MR ionogel. The figures also show that the MR ionogel samples with higher polymer fraction exhibits growing shear stress difference under the augmented curing magnetic field, as the aforementioned saturation is delayed with the increase of the curing magnetic field. Moreover, there exists an increasing trend of the pre-yield region with the increasing fraction of polymer addition and increasing curing magnetic field, which is due to a more established internal microstructure. This is a welcomed phenomenon, as elastomeric magnetorheological material, like this proposed MR ionogel, generally works in the pre-yield region, whereas magnetorheological fluids (MRFs) mostly operate in the post-yield region. These results are also observed in the dynamic oscillatory strain sweep tests for MR ionogel samples cured at various curing magnetic fields, where increased modulus values and extended LVE range are observed as well, as shown in Figure 8.10(a)-(c).
Chapter 8 A novel class of ionogels with a controlling structure based on Magnetorheology

(a)

(b)

(c)
Figure 8.9 Steady shear experiment of MR ionogel sample (a) A, (b) B and (c) C fabricated under various curing magnetic fields.
Figure 8.10 Oscillatory dynamic strain sweep experiment of MR ionogel sample (a) A, (b) B and (c) C fabricated under various curing magnetic fields, $\omega = 5 \text{rad/s}$

The relevance between the rheological behaviour of the MR iongel samples and the curing magnetic field may be attributed to the permanent formulation of dipolar magnetic nanoparticles that align as the samples are cured under both UV light source and curing magnetic field:

When no magnetic field is applied during fabrication, the magnetic particles would distribute randomly in the ionogel network, thus contributing minimum variation to the overall mechanical properties of the MR iongel samples. However, when an external curing magnetic field is applied, the magnetisable nanoparticles would acquire a certain amount magnetic moment which would compete against the thermal force and the interaction between the ionogel matrices, thus be adopted in a directionally ordered anisotropic alignments. These alignments following the direction of external magnetic field would be considered a fortifying structure for the MR iongel samples that results in increased shear stress response. Moreover, as the curing magnetic field grows, the magnetic force would become overwhelming and all the magnetic nanoparticles are included in the field-induced magnetic structure. As a result, the shear stress would reach a maximum value and no longer increase, such
saturation phenomenon is shown and conformed to the overlapping shear stress curves at relatively higher curing magnetic fields (Figure 8.9(a)-(c)).

As for the fact that the MR ionogel samples with growing polymer addition exhibit increased stress difference with respect to increasing curing magnetic field, this phenomenon could be attributed to the increased resistance of polymer network against the magnetic force, which leads to the delay of shear stress saturation. Consequently, we could come to the conclusion that a wider range of manipulation on the mechanical properties of MR ionogel may be expected when fabricated in softer matrices.

In summary, the rheological behaviour of MR ionogel samples fabricated under various curing magnetic fields demonstrate an obvious affinity to structural variation, and a coupling effect of the field-induced magnetic structure and the polymer network is observed, which would ensure operational stability and resistance to external deformation of MR ionogel samples.

**MR effect of MR ionogel**

Beside the contribution made by the curing magnetic field on the magnetic structure and its affinity in mechanical properties, another significant feature of MR ionogel is its controllability with respect to in-use external magnetic fields. Therefore, rheological tests are also carried out to examine the MR effect of MR ionogel.

The steady shear comparison of isotropic MR ionogel A0, B0, and C0, and the anisotropic MR ionogel A240, B240, and C240 is presented in Figure 8.11(a)-(f). The figures indicate that all the MR ionogel samples experience some increase in shear stress as the external magnetic field increases, which illustrates their sensitivity to an external magnetic field, namely, the MR effect. The MR effect is usually evaluated by the scaling parameter defined by the ratio of shear stress under maximum external magnetic field and zero-field shear stress within the pre-yield region of the MR ionogel samples. This parameter is calculated and listed in Table 8.1. The scaling parameter is related to the microstructure of the MR ionogel, as the specific values for the anisotropic samples are larger than those for isotropic samples. Besides, the scaling parameter also exhibits an increasing trend with respect to the amount of
polymer addition, which indicates that the increasing amount of polymer addition of MR ionogel could lead to a more pronounced MR effect. Moreover, as could be observed from the resultant shear stress curves in Figure 8.11, the pre-yield region increases slightly as the amount of polymer increases.

The MR effect for the MR ionogel samples is related to a dipolar interaction of the structured (random distribution for isotropic samples) magnetic particles that causes a closer and stronger bond between them when an increasing external magnetic field is applied to the MR ionogel samples. As a result, the increasing external magnetic field would provide an increasing magnetic force which requires much more effort to twist and deform the field defined magnetic structures.

The ascending trend of scaling parameter for anisotropic MR ionogel samples could be explained by the fact that internal dipolar magnetic alignments are in the same direction as the external magnetic field. While the random distribution of magnetic particles in isotropic MR ionogel samples would lead to some cancellation effect, which could weaken the effect of magnetic force, as evidenced by the reduced scaling parameters for isotropic MR ionogel.

Moreover, the extended pre-yield region for MR ionogel with increased amount of polymer proves that MR ionogel samples based on softer and more flexible ionogel matrix would exhibit a more pronounced MR effect, and thus a better adoption of magnetic particle structures within ionogel matrix network and more applicable solid electrolyte materials from the prospective rheological assessment.

(a)  
(b)
Figure 8.11 MR effect of isotropic MR ionogel (a, c, e) A0, B0, C0 and anisotropic MR ionogel (b, d, f) A240, B240 and C240 in steady shear experiment

Table 8.1 Scaling factors used to evaluate the MR effect of isotropic and anisotropic MR ionogel samples

<table>
<thead>
<tr>
<th>Isotropic sample</th>
<th>scaling parameter</th>
<th>Anisotropic sample</th>
<th>scaling parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR ionogel A0</td>
<td>1.08</td>
<td>MR ionogel A240</td>
<td>2.45</td>
</tr>
<tr>
<td>MR ionogel B0</td>
<td>5.84</td>
<td>MR ionogel B240</td>
<td>7.77</td>
</tr>
<tr>
<td>MR ionogel C0</td>
<td>8.87</td>
<td>MR ionogel C240</td>
<td>9.29</td>
</tr>
</tbody>
</table>
Figure 8.12 MR effect of isotropic MR ionogel (a, c, e) A0, B0, C0 and anisotropic MR ionogel (b, d, f) A240, B240 and C240 in dynamic oscillatory strain sweep experiment.

The dynamic oscillatory strain sweep tests with a constant angular frequency of 5 rad/s are presented in Figure 8.12(a)-(f), where the dynamic rheological behaviour with regards to the external magnetic field is similar to that of steady shear experiment.
8.4 Conductivity of MR ionogel

Impedance test between two quadrilateral gold mylar electrodes is carried out to determine the conductivity of the MR ionogel samples (cut into 20mm diameter discs beforehand). The conductivity value was calculated using the equation

\[ \alpha = \frac{L}{AR_c} \]

Where \( L \) is the gap between the electrodes, \( A \) is the conductive area, and \( R_c \) is the resistance value at the highest frequency in the impedance test.

The conductivity test results for MR ionogel samples are summarised in Table 8.2, where MR ionogel A grows from 3.78mS/cm to 4.22mS/cm, MR ionogel B grows from 3.31mS/cm to 3.96mS/cm and MR ionogel C grows from 2.23mS/cm to 3.7 mS/cm, as the curing magnetic field increases from 0 to 240mT. Consequently, one could observe a clear increasing trend of conductivity with the increase of the curing magnetic field, under which the MR ionogel samples are fabricated. Furthermore, similar to that is observed in rheological test result, the conductivity values of the MR ionogel samples also exhibit saturation at growing curing magnetic field, as the increase of the conductivity values slows down with the increase of curing magnetic field. Besides, a delayed saturation could also be noticed with greater fraction of polymer addition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (mS/cm)</th>
<th>Sample</th>
<th>Conductivity (mS/cm)</th>
<th>Sample</th>
<th>Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR ionogel A0</td>
<td>3.78</td>
<td>MR ionogel B0</td>
<td>3.31</td>
<td>MR ionogel C0</td>
<td>2.23</td>
</tr>
<tr>
<td>MR ionogel A60</td>
<td>3.98</td>
<td>MR ionogel B60</td>
<td>3.47</td>
<td>MR ionogel C60</td>
<td>2.35</td>
</tr>
<tr>
<td>MR ionogel A120</td>
<td>4.12</td>
<td>MR ionogel B120</td>
<td>3.60</td>
<td>MR ionogel C120</td>
<td>2.99</td>
</tr>
<tr>
<td>MR ionogel A240</td>
<td>4.22</td>
<td>MR ionogel B240</td>
<td>3.96</td>
<td>MR ionogel C240</td>
<td>3.43</td>
</tr>
</tbody>
</table>

The observed increasing trend of conductivity according to the increase in the curing magnetic field could be explained this way:
When a curing magnetic field is not applied or is small, there is competence between the directional magnetic force that led to an orderly alignment and a thermal force that favored a random distribution of magnetic particles. Consequently, many magnetic particles end up drifting in the ionogel matrix, despite the formulation field-induced microstructure. Such resultant uncertainty in the microstructure would hinder ionic motion and reduce conductivity. As the curing magnetic field begins to increase, the magnetic force gradually dominates the orientation of magnetic particles during the fabrication process as more and more magnetic particles are incorporated into the aggregates of field-induced microstructure and gives way to a smoother pathway for ion transportation. The increase in conductivity would be expected as a result. When the curing magnetic field becomes so large that all the magnetic particles are adopted in field-induced microstructure, conductivity of MR ionogel would be saturated and no longer increases, as microstructure uncertainty is completely decoupled from ion transportation.

A field-on conductivity test is also conducted on the isotropic MR ionogel and anisotropic MR ionogel which fabricated under a curing magnetic field of 240 mT to determine conductivity evolution of MR ionogel samples incorporating permanent dipolar magnetic structures when an in-use magnetic field is applied. Two permanent magnets are placed on either side of the samples and a magnetic field of approximately 100mT is applied. The field on conductivity experiment exhibits a slight increase upon the application of in-use magnetic field, which is listed in Table 8.3. This result proves that the MR ionogel samples shouldn’t stir any concerns upon in-use magnetic field.

| Table 8.3 Comparison of field on and field off conductivity test results for MR ionogel samples | 156 |
## Table 8.3 Conductivity of MR Ionogels with Magnetic Field On/Off

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (mS/cm) Field off</th>
<th>Conductivity (mS/cm) Field off</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR ionogel A0</td>
<td>3.78</td>
<td>3.84</td>
</tr>
<tr>
<td>MR ionogel A240</td>
<td>4.22</td>
<td>4.31</td>
</tr>
<tr>
<td>MR ionogel B0</td>
<td>3.31</td>
<td>3.41</td>
</tr>
<tr>
<td>MR ionogel B240</td>
<td>3.96</td>
<td>4.05</td>
</tr>
<tr>
<td>MR ionogel C0</td>
<td>2.23</td>
<td>2.37</td>
</tr>
<tr>
<td>MR ionogel C240</td>
<td>3.43</td>
<td>3.64</td>
</tr>
</tbody>
</table>

The increasing trend of conductivity for MR ionogel samples during the field on test could be attributed to minor movement of the magnetic particles following the direction of the applied magnetic field that is in line with the dipolar alignments of the anisotropic MR ionogel samples. This movement would lead to a growing fraction of conductive components inside the MR ionogel material, thus lead to a slight increase in conductivity. Considering that the MR ionogel samples are solid and free standing with a well-defined shape, such a movement should be quite small without causing any significant macro deformation. This increasing trend may be more obvious in relatively softer material which allows the embedded particles to move more easily. As shown in Table 8.3, MR ionogel C has the largest conductivity difference upon in-use magnetic field, and MR ionogel A has the smallest value.

A review of the conductivity test of the MR ionogel samples would lead to the conclusion that the proposed MR ionogel possessed high conductivity that could be conveniently pre-defined by manipulating the curing magnetic field during fabrication. Moreover, according to the field on conductivity test, the evolving conductivity of MR ionogel samples followed the same trend as the strengthening effect of the external magnetic field which successfully identified the MR concept to ionogel research. The fact that MR ionogel was both highly conductive and precisely responsive to external magnetic fields means that the current research opened an avenue for fabrication of novel ionogel, which could also be considered a
multifunctional MRE.

### 8.5 Microscopic observation of MR ionogel

Microscopic observation was undertaken with a Leica M205 A optical microscopy to observe the microstructure of MR ionogel samples, and to connect the microstructure of MR ionogel samples to the physical properties determined in these aforementioned physical experiments.

The microscopic observation of exemplified MR ionogel samples A0, A120 and A240 is presented in Figure 8.13(a)-(c), and it would serve as direct evidence to explain the properties of MR ionogel samples. There was a random distribution of magnetic particles with isotropic samples and an orderly alignment of magnetic particles with the anisotropic samples; these structural differences caused the physical properties of the proposed MR ionogel to evolve, as has already presented in previous subsections.
8.6 Conclusion

In this chapter, a magnetorheological ionogel (MR ionogel) is proposed by building a field controlled magnetic structure in a UV cross linked ionogel matrix material. The evolution of rheological properties and conductivity of MR ionogel samples are examined and analysed in detail. Featuring the field controllable mechanical and conductive property, as well as significant field responsive mechanical property upon in-use application of magnetic field, this proposed MR ionogel may be considered as a novel high performance solid electrolyte that could be tailored for various applications in the development of flexible wearable solid electronic devices. Moreover, being a dual functional elastomeric MR material demonstrating sound controllable mechanical strength and conductivity, this MR ionogel should also have huge potential in the design of active actuator and high precision sensor.
Chapter 9 Conclusions

9.1 Contribution

The major contribution in this thesis is to explore a pathway of developing new soft materials by adopting active and/or passive controllable structures, so as to improve the physical properties, for instance, mechanical strength and conductivity. Several novel materials are derived as a result of this, including MR shear thickening fluid (MRSTF), Ionic liquid shear thickening fluid (ILSTF), MR electrolyte and MR ionogel.

Comprehensive experimental investigation and modelling approach are applied to the development of magnetorheological shear thickening fluid (MRSTF), which exhibits both reactive and pro-active mechanical property variation upon rapid shear loading and controlling magnetic field, respectively.

The concept of shear thickening and magnetorheology were also introduced to unique conductive medium of ionic liquid.

The ionic liquid shear thickening fluid (ILSTF) was found to acquire shear thickening phenomenon and transform to a viscoelastic composite from the original Newtonian liquid by dispersing fumed silica nanoparticles, which allows better protection mechanism against mechanical abuse. This welcome change was realized with improved conductivity at certain fraction range.

The MR electrolyte was generated by dispersing magnetic nanoparticles to highly conductive ionic liquid with the silica-ionic liquid composite structure also applied to ensure the sedimentation stability of the MR electrolyte. This magnetic field sensitive liquid electrolyte was reversible and switchable between liquid and solid phase; which transition was staged without obvious conductivity decrease. This unique property allowed the MR electrolyte to work in a solid state upon request without sacrificing performance, in case extra resistance against external impact was required.

The MR ionogel was a derivative of its liquid counterpart, which was fabricated by
embedding structured magnetic particles in UV initiated ionogel matrices. There are several benefits for the MR ionogel.

First of all, the structure of magnetic particles arrangement could be manipulated by various types of magnetic field, thus allowed controlling of conductivity through magnetic field, which was a more feasible method than polymer orientation control that requires complex facilities.

Secondly, the permanently locked structure of MR ionogel didn’t require an extra magnetic system like its liquid counterpart. Besides, as supported by conductivity tests undertaken under field condition, the application of magnetic field during usage wouldn’t cause any negative effect on the overall performance of the novel solid electrolyte, but slight conductivity increase was recorded.

Thirdly, with the magnetic particle structure playing the backbone role in this solid material, the fraction of conductive component of MR ionogel was much higher than existing solid polymer electrolytes (SPEs) with well-defined field responsive mechanical properties, which improved the adoption of MR ionogel in novel light-weighted durable high performance electrochemical devices comparing to existing SPEs.

Besides, the elastomeric MR ionogel with embedded of magnetic particle structure allowed possible multifunctional application, as it was both conductive and responsive of external magnetic fields.

9.2 Future work

Study the structure affined conductivity

As stated in previous section, magnetic field was proved to play a critical role in building the magnetic structure in the MR ionogel systems, which would allow effective manipulation of their physical properties. Consequently, various conductivity and/or mechanical properties could be derived as a result of different types of curing magnetic fields, for instance, constant magnetic field and alternating magnetic field. The straightforward fabrication process and precisely controlled
physical properties would allow broad customize of the field responsive conductive material for specific technological concerns.

*The application of MR ionogel as novel MR elastomer (MRE)*

The elastomeric MR ionogel material may be considered as a novel MRE generated in a unique platform of ILs, as pronounced MR effect could be observed. The fact that the MR ionogel possessed precisely determined conductivity would lead to multiple source of control of the smart material in actual engineering applications.

*Biomechanical properties of the MR ionogel*

The MR ionogel was generated by adopting magnetic structure to conductive medium, thus made it possible to apply it as novel actuator that facilitate both electrical and magnetic control. Consequently, by combining controlling strategies of both mode, the actuator’s motion would be in a much more controlled and precise fashion.
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