Field-Dependent Viscoelastic Properties of Graphite-based Magnetorheological Grease

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ABSTRACT – This paper highlights the effect of graphite on the dynamic viscoelastic properties of magnetorheological grease (MRG). Two types of MRG namely MRG and graphite-MRG, GMRG with 0 wt.% and 10 wt. % of graphite respectively was synthesized by using a mechanical stirrer. The rheological properties of both samples at various magnetic field strengths from 0 to 0.603 T was analyzed via rheometer under oscillatory mode with strain ranging from 0.001 to 1% with fixed frequency at 1 Hz for strain sweep and frequency ranging from 0.1 to 80 Hz at a constant strain of 0.01 % for frequency sweep. Based on the result obtained, the value of storage and loss modulus are dependent on the graphite content. A high value of storage modulus was achieved in the GMRG sample at all applied magnetic field strengths within all frequency ranges. These phenomena related to the contribution of graphite to forming the chain structure with CIPs and offered a more stable and stronger structure as compared with MRG. Moreover, the reduction in the value of loss modulus in GMRG was noticed compared to MRG at on-state condition reflected by the high value of storage modulus, G′ acquired compared to loss modulus, G″ at all frequency ranges. Therefore, the utilization of graphite in MRG can be used in wide applications such as brake and seismic dampers.

INTRODUCTION

Magnetorheological grease (MRG) is a type of smart material due to its rheological properties that can be controlled with the influence of magnetic fields [1-3]. MRG is comprised of magnetic particles usually carbonyl iron particles (CIPs) that are dispersed in the grease medium. It was first discovered in 1999 to overcome the sedimentation issues in Magnetorheological fluid (MRF) by replacing a thin viscosity suspension medium with a more thick suspension grease that are dispersed in the grease medium. It was first discovered in 1999 to overcome the sedimentation issues in Magnetorheological fluid (MRF) by replacing a thin viscosity suspension medium with a more thick suspension grease that are dispersed in the grease medium. It was first discovered in 1999 to overcome the sedimentation issues in Magnetorheological fluid (MRF) by replacing a thin viscosity suspension medium with a more thick suspension grease that are dispersed in the grease medium. Ahamad et al. [4] stated that the properties of MRG are in between MRF and Magnetorheological elastomer (MRE). The reason for that is because, grease is a type of non-Newtonian liquid with yield stress, therefore it can hold with the influence of magnetic fields [1-3]. MRG is comprised of magnetic particles usually carbonyl iron particles (CIPs) to MRE [5]. Aside from those listed above, utilizing grease as a medium has offered several benefits in MRG such as the CIPs in MRE that are fixed in a solid rubber matrix [6]. Therefore, a higher MR effect was recorded in MRG compared to MRE [5]. Aside from those listed above, utilizing grease as a medium has offered several benefits in MRG such as self-sealing properties, robustness in high temperature and pressure, anti-wear properties as well as reduced friction due to their lubricant properties [2,7]. Because of its outstanding properties, several applications such as seismic damper, brake, clutch and engine mounts can potentially be applied by using MRG [5]. Despite that, a previous study stated that the performance of MRG is still low compared to MRF because, although the CIPs are freely moving within the medium, yet the movement was hampered [8]. Therefore, a great number of extensive work was implemented to improve the rheological properties of MRG, and one of the methods is by utilizing additives.

Generally, additives are the addition of elements within a small range between 0.1-15 wt% in the polymer material purposely to enhance its properties [9]. There are several types of additives that have been implemented in MRG which can be categorized under liquid or solid-based. A study done by Kim et al. [1] had utilized 5 wt% kerosene oil in MRG and reported that the off-state viscosity of MRG can be reduced which led to an improvement of the CIPs’ mobility in the medium with an application of the magnetic fields. Nevertheless, the viscoelastic properties and yield stress of MRG was notably to be dropped. A similar finding was found in [10] that utilized and compared the rheological performance of MRG with three distinct types of dilution oil; kerosene, castor and hydraulic oil. The study revealed that the employment of these three types of dilution oil by up to 15wt% can reduce the off-state viscosity of MRG, yet the yield stress and viscoelastic properties of MRG show a remarkable decrease in their value. The phenomenon occurred because, the addition of dilution oil in MRG causes the CIPs to become less adhered to the medium, and via application of shear,
it will tend to undergoes a slippery effect. Therefore, the formed chain structure by CIPs with influence of magnetic field is not stable and required high magnetic field strength to form a stable polarized chain structure. Consequently, these reduced the performance of MRG. Moreover, the author also mentioned that by addition of more than 10 wt.% dilution oil led to decreased stability of the MRG. Aside from that, a few solid based additives in nano-sized that have been introduced in MRG are chromium dioxide, CrO2 [11] and superparamagnetic γ-Fe2O3 [12]. Based on the outcome, it can be concluded that utilizing nanoparticle additives able to improve the stability of low viscosity MRG and at the same time lowering the viscosity of MRG at the off-state condition. Even so, it does not bring any significant enhancement in terms of yield stress and viscoelastic properties of MRG. The reason for that is because, as stated by Leong et al. [13] the CIPs chain in MRG does not affect by the employment of nanoparticle additives. Thus, nanoparticles addition does not contribute to the formation of strong and stable chain structures in MRG.

From the previous related study, we can deduce that additives that has been employed in MRG mainly able to reduce the off-state viscosity of MRG, yet its yield stress and viscoelastic properties are either maintained or reduced. Viscoelastic properties are also an important parameter to be considered before a material is applied in an application. Hence, this paper presents a new type of additives that can enhance the viscoelastic properties of MRG. Aside from additives that have been listed above, carbon-based additive, graphite was another potential additive that can be utilized in MRG. Numerous studies have proved that the utilization of graphite gives a remarkable enhancement of the properties in MR material in terms of electrical [14]–[18], tribological [19] and also rheological properties [15-16,20-21]. Research done by Tian et al. [21] found that the initial mechanical properties of MRE were seen to enhance by the employment of graphite due to the contribution of graphite toward forming more stronger structure in MRE. Then, Pang et al. [16] also noticed that the addition of 15 wt.% graphite in MR plastomer (MRP) improved the saturated storage modulus by up to 0.8 MPa compared to pure MRP. Furthermore, a study done by Shabdin et al. [15] has disclosed that the addition of graphite in MRE improved the storage modulus and loss factor of the MRE. Besides, the MR effect of MRE was also escalated by up to 60 % compared to the conventional MRE. Recently, Thakur et. al [20] discovered that the value of shear stress and yield stress of MRF was significantly enhanced through the addition of graphite by up to 3 wt.% addition. It can be concluded that graphite is able to aid in the development of chain structure with CIPs to create a more strong structure via the influence of magnetic fields. Hence, the present study utilized graphite as an additive in MRG (GMRG) and their rheological properties in terms of dynamic viscoelastic are investigated and compared with pure MRG.

**EXPERIMENTAL**

**Materials**

Magnetic particles used in the present study are carbonyl iron particles, CIPs from BASF, OM grade, with a size of 5 μm and density of 7.874 g/cm³. While the suspension medium utilized in this study is commercial grease from NPC Highrex HD-3 Grease, Nippon Koyu Ltd. Japan. The density and viscosity of the utilized grease are 0.92 g/cm³ and 190 cSt respectively. Moreover, the additives that being employed are graphite from R&M Chemicals, with an average size of 16 μm and density of 1.8 g/cm³. The fabrication process of MRG and GMRG were illustrated in Figure 1. Initially, grease was stirred for 5 minutes by a high-speed mechanical stirrer (HD-30D, DAIHAN Scientific Co., Ltd) to open its fibrous structure. Afterwards, either CIPs or CIPs and graphite were added together into the stirred grease and the mixture was continually stirred for additional 2 hours in order to achieve a homogenized mixture. Table 1 displayed the percentage by weight of each composition in both samples.

| Sample | Grease | CIPs | Graphite |
|--------|--------|------|----------|
| MRG    | 30     | 70   | 0        |
| GMRG   | 20     | 70   | 10       |

**Characterization**

The dynamic viscoelastic properties of both samples, MRG and GMRG were analyzed and compared through Modular Compact Rheometer (MCR 302). The rheometer was equipped with electromagnetic (MRD 70/1T) to produce magnetic fields. A parallel-plate measuring system with a 20-mm diameter and 1-mm gap was applied in the present study. Both samples were examined under oscillatory mode with a strain range from 0.001 to 10% at a fixed frequency of 1 Hz and frequency ranging from 0.1 Hz to 80 Hz under a constant strain of 0.01%. The magnetic field strength applied for each test was varied from 0 to 0.603 T by adjusting the coil applied current from 0 to 3 A. The applied current of 0 A, 1 A, 2 A, and 3 A corresponded to the magnetic field strength of 0, 0.212, 0.418, and 0.603 T respectively. Noted here that all experiment was conducted at room temperature.
EXPERIMENTAL RESULTS

In order to understand the viscoelastic behavior of MRG, rheological analysis under oscillatory mode with varied strain and frequency range need to be carried out. The viscoelasticity behavior of MRG basically was studied through storage ($G'$) and loss ($G''$) modulus [22]. Storage modulus refers to the elastic behavior of the samples that depends on the formation of a chain-like structure and is related to energy storage [23]. Meanwhile, loss modulus, $G''$ refers to the viscous behavior of the material that is related to the energy dissipation and determines the fluid-like characteristic of the material [23]. Figure 2 represents the analysis of the sample under strain varied from 0.001 to 10 % at different magnetic field strengths.

**Figure 1.** Fabrication process of MRG and GMRG.
The strain sweep was firstly performed to indicate the linear viscoelastic (LVE) region of the samples [24]. From the result obtained, it is observed that both samples show a similar trend whereas, the storage modulus, G’ exhibits a plateau region and shows a non-linear trend after passing a specific value of strain known as critical strain [25]. Noted here, microstructural damage was experienced by all samples after passing through the critical strain [26]. Therefore, it is crucial to identify the LVE region which is the region before the critical strain prior to further analyzing the sample without damaging it [23]. From the result obtained, the LVE region was denoted at 0.01 %. From the acquired LVE region, a frequency sweep was performed at a varied range of frequencies at a fixed strain of 0.01% to gain information regarding the structural organization of the sample’s suspension at a wide range of frequencies. Figure 3 illustrates the effect of frequency on the storage modulus, G’ at different applied magnetic field strengths.

Both samples demonstrated a similar trend whereas the storage modulus was dependent on frequency and display a linear increment below 10 Hz. The acquired trend was usually remarked in a high entangled polymeric system and was similar to a standard lubricating grease [27,28]. An increment of the storage modulus is reflected in the improvement of elasticity by both samples which leads to an achievement of stable and stronger structure [29]. Nevertheless, after the initial period (>10 Hz), the storage modulus, G’ of both samples exhibits a plateau region along with the increasing frequency at a constant magnetic field which is attributed from the fast movement of the vane that inhibits the system to relax via viscous flow [27]. The elastic plateau region presented a strong solid-like structure gained in MRG and GMRG [30]. Moreover, it was seen that the storage modulus, G’ of both samples increase along with escalated magnetic field strength at all frequency ranges. These have corresponded to the formation of stronger columnar chain structures at high magnetic fields with the influence of frequency resulting from the dipole-dipole interaction between the CIPs [31]. Furthermore, the result also displayed that the storage modulus, G’ of MRG was dependent on the addition of graphite. The storage modulus, G’ of GMRG presented a higher value than the MRG sample at all frequency range from 0.1 to 80 Hz either in off-state and on-state condition. The phenomena related to the better elasticity exhibited in the GMRG sample.
due to the presence of graphite which strengthened the interconnection between CIPs in the GMRG sample. As a consequence, GMRG’s suspension will develop more structural network density and results in high stiffness [32].

Additionally, Figure 4 displayed the effect of frequency on the loss modulus, $G''$ of MRG and GMRG at various applied magnetic field strengths. The results show that the loss modulus, $G''$ for both samples were dependent on the frequency and exhibit a linear increment along with an increasing frequency range from 0.01 to 80 Hz at the off-state condition. Besides, the GMRG exhibited a higher value of loss modulus compared to MRG due to its high structural network density which contributed from the presence of additional graphite particles [27]. Nonetheless, with the presence of magnetic fields, the loss modulus, $G''$ for both samples shows nearly independent with frequency. The reason for that is because, without the influence of magnetic field, the particles in the samples are randomly distributed and no formation of stable structures are formed at this stage. The particles only collide with one another under shearing process and heat were produced resulting from the friction occurring between the particles [33]. Then, more heat was dissipated at a high frequency due to the increasing number of collisions that were expected to happen. In contrast to the off-state condition, the loss modulus, $G''$ of both samples in the on-state condition displayed a nearly flat trend at all frequency ranges and the value of loss modulus, $G''$ for each sample was seen to decrease along with escalated magnetic field strength. This is due to the formation of polarized chain structures that are developed with the influence of magnetic fields and much strong and stable structures were formed by increasing the magnetic field strength. As a result, it will resist the structural damage from occurring via oscillatory shear [33].

![Figure 4. Loss modulus, $G''$ of MRG and GMRG as a function of frequency at varied applied magnetic field strength.](image)

In contrast to the off-state condition, the loss modulus, $G''$ of GMRG was observed to have a lower value compared to the MRG at the on-state condition indicating that, low heat was dissipated in GMRG due to the present of graphite that contributes towards formation of strong and stable chain structure along with increasing of magnetic fields strength. Aside from that, it is noticed that the loss modulus, $G''$ for GMRG at 2 A and 3 A applied current shows a minimal decreasing trend at low frequency (<40 Hz). Based on the stable storage modulus, $G'$ values shown in Figure 2, these occurrences might attributed from the adjustment of its microstructure rather than the demolition of its microstructure [34]. In overall, compared to the value between storage, $G'$ and loss modulus, $G''$ of both samples, it is shown that storage modulus, $G'$ present a higher value than loss modulus, $G''$ at all frequency ranges. These indicate strong solid-like (elastic) properties displayed by both samples.

**CONCLUSION**

Two types of MRG namely MRG and GMRG with a constituent of 0 wt.% and 10 wt.% of graphite respectively were fabricated through a direct mixing process by mechanical stirrer. The rheological properties of GMRG were examined and compared with MRG via rheometer under oscillatory mode. From the finding result, the LVE region was remarked at 0.01 % under strain sweep. Moreover, based on the frequency sweep result that was conducted at a frequency range from 0.1 to 80 Hz, it shows that, the storage modulus, $G'$ of GMRG exhibits a higher value compared to MRG along with elevated applied magnetic field strength at all frequency range. Meanwhile, the loss modulus, $G''$ of GMRG seem to have a lower value compared to the MRG sample reflecting that a more stable structure was achieved in GMRG compared with MRG at the on-state condition. Furthermore, the value of storage modulus (elastic) was overhead the value of loss modulus (viscous) shows that both samples exhibit strong solid-like (elastic) behavior.

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