Effect of Plasticizer on Microstructure and Dynamic Mechanical Performance of Anisotropic Magnetorheological Elastomers

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Abstract. Anisotropic magnetorheological elastomers (MREs) based on natural rubber and industrial waste nickel zinc ferrite were prepared. Paraffin oil was employed as plasticizer to modify the viscosity of rubber matrix. The amount of plasticizer was varied at five levels (5, 10, 20, 30 and 40 phr) to assess the ability of nickel zinc ferrite particles to align into chain like columnar structures within the rubber under an applied magnetic field. Scanning electron microscopic (SEM) and dynamic mechanical analysis over frequency range of 1-100 Hz and a strain amplitude range of 0.1-6% were examined. SEM micrographs revealed that the chain like columnar structures become longer and thicker as the viscosity of the rubber matrix decreased. It was found that 5 phr plasticizer produced the highest tan δ over the range of frequency and strain amplitude explored.

Keywords: Natural rubber; Waste nickel zinc ferrite; Magnetorheological; Plasticizer; Paraffin oil

1. Introduction

Magnetorheological elastomers (MREs) consist of magnetic particles and an elastic polymer matrix such as soft silicone elastomers, poly vinyl alcohol, gelatin, hard natural rubber and polychloroprene rubber[1]. The magnetic particles that are usually used in MREs are carbonyl iron and iron oxide [2]. MREs can be fabricated into isotropic MREs and anisotropic MREs. Isotropic MREs can be characterized by having uniform dispersion of magnetic particles embedded in the rubber matrix. Anisotropic MREs have a formation of chain like structure within the rubber matrix resulting from subjecting the materials to an external magnetic field [3]. Anisotropic MREs are found to produce materials with larger stiffness and better dynamic properties [4, 5].

Fabrication of MREs needs a lot of attention and consideration, not only in selection of the magnetic particles, but the performance of MREs also depends on matrix viscosity of rubber. MREs with different matrix viscosity are believed to have a significant effect on the ability of particles to orientate along the magnetic field direction [6]. Anna et al. found that anisotropic MREs based on silicone rubber with viscosity of 30 000 mPa.s and carbonyl iron has limited oriented structure of particle chain in the rubber matrix [7, 8]. Jung et al. reported that MREs based on natural rubber with viscosity of 81.10 mPa.s and carbonyl iron has good alignment and good dynamic properties [9, 10].

In this study, anisotropic MREs based on waste nickel zinc ferrite and natural rubbers were prepared. The viscosity of rubber matrix was modified using plasticization method [11]. The effect of matrix viscosity on magnetic particle alignment in the rubber matrix was investigated by scanning electron microscopy and dynamic mechanical testing over a range of frequency and strain amplitude. The loss tangent (tan δ) was considered as the fundamental parameter to assess dynamic performance. Tan δ gives a comparison of the energy lost to that stored; it is obtained by dividing the loss modulus (G΄΄) by the storage modulus (G΄).
2. Materials and Methods

2.1 Materials

The anisotropic MREs sample was prepared by compounding waste nickel zinc ferrite and natural rubber. The compound formulation used in this study is listed in Table 1. Natural rubber and compound ingredients such as zinc oxide, stearic acid, paraffin oil, n-cyclohexyl-2-benzothiazole sulfonamide (CBS), tetramethylthiuram disulfide (TMTD), sulphur and n-isopropyl-n’-phenyl-p-phenylenediamine (IPPD) were purchased from Zarm & Chemical Supplier Sdn. Bhd. Waste nickel zinc ferrite was obtained from ACME Ferrite Products (M) Sdn. Bhd.

Table 1. Formulation of rubber compound

| Materials                  | Function      | Loading (phr) |
|----------------------------|---------------|---------------|
| Natural rubber             | Matrix        | 100 100 100 100 100 100 |
| Zinc oxide                 | Activator/peptiser | 5 5 5 5 5 5 |
| Stearic acid               | Activator/peptiser | 1 1 1 1 1 1 |
| Paraffin oil               | Plasticizer   | 0 5 10 20 30 40 |
| Waste Nickel Zinc Ferrite  | Filler        | 70 70 70 70 70 70 |
| CBS                        | Accelerator   | 2 2 2 2 2 2 |
| TMTD                       | Accelerator   | 1 1 1 1 1 1 |
| Sulphur                    | Crosslinking agent | 1.5 1.5 1.5 1.5 1.5 1.5 |
| IPPD                       | Antioxidant   | 2 2 2 2 2 2 |

2.2 Sample Preparation

In this study, mixing process was carried out on a conventional laboratory two roll mill size 160 x 320 mm (model XK150) according to ASTM designation D 3184-80. The compounding began with softening the rubber (mastication) about 2-3 min. The additives in Table 1 (other than accelerators and sulphur) were then added followed by nickel zinc ferrite; addition of accelerators and sulphur were delayed to the last part of the process to prevent premature vulcanization during compounding. The cure time, $t_{90}$ at 150 °C was then determined using Monsanto Rheometer, Model MDR 2000 (moving die rheometer) according to ISO 3417. 37 g of rubber compound was placed in a mould 124x 70x 3 mm. The anisotropic MREs were pre-cured to an external magnetic field in a specially developed magnetic mould at 80 °C for 30 min. The particles were magnetized, and then form chains aligned along the field direction and subsequently were cured in a compression moulder at 150 °C under a pressure of approximately 12 MPa.

2.3 Viscosity

The viscosity test was performed using parallel plate rheometer (Physica, MCR 301). The spindle type of parallel plate rheology are plate PP25. The viscosity test was performed on a circular specimen of 20 mm diameter and 3mm thickness in shear mode at room temperature.
2.4 Dynamic Mechanical Properties Measurements
A dynamic mechanical property of rubber composites was performed using parallel plate rheometer (MCR 302, Anton Paar Company, Germany). The spindle type of parallel plate are plate PP25. The dynamic measurements were performed under room temperature through oscillatory amplitude and frequency sweep procedure. Tan δ was measured over the frequency range of 1-100 Hz at a fixed strain amplitude range of 0.1-6% at a fixed frequency of 10 Hz.

2.5 Scanning Electron Microscope (SEM)
The fracture surface of the MREs was observed by using scanning electron microscope (SEM), SUPRA ™35-V, ZEISS USA. The micrograph obtained from SEM can be used to observe the filler distribution in the matrix with an accelerating voltage of 20 kV. The fracture ends of the sample were mounted on aluminium stubs. Then, the sputter coated with a thin layer of gold to avoid electrostatic changing and poor resolution.

3. Results and Discussion
3.1 Viscosity of rubber matrix
Viscosity of MREs at different contents of plasticizer is shown in Fig. 1. The viscosity test measure material resistance to flow. The viscosity decreased with increasing plasticizer contents. This effect could be explained due to reduction in cohesive attraction force between polymer chains when paraffin oil molecules penetrate into the rubber matrix. Addition of plasticizers into the rubber matrix also enhance the sliding of rubber molecular chains. This effect could potentially enhance the arrangement of magnetic particles during curing under an applied magnetic field and potentially increase the magnetism induced damping of the MREs [12].

![Viscosity of MREs at different contents of plasticizer](image)

**Fig. 1.** Viscosity of MREs at different contents of plasticizer

3.2 Scanning electron microscope (SEM)
SEM micrographs of MREs with different plasticizer content are shown in Fig. 2. As can be seen for MRE without plasticizer, the waste nickel zinc ferrite particles was not well organized into chain like columnar structure as a consequence of curing the material under an applied magnetic field at elevated temperature. For MREs with addition of plasticizer, It can be seen that the waste nickel zinc ferrite chains get dense, longer, and the gap between the adjacent chains decreased as
the plasticizer content increased from 5 to 40 phr. Thickness and length of the magnetic particle chain are tabulated in Table 2. Clearly, the thickness and length of waste nickel zinc ferrite increased as the plasticizer content increased. It is expected that increase magnetic particle interaction of waste nickel zinc ferrite by using plasticizer could further enhanced the dynamic performance of MREs. However, there are a lot of cavities remaining due to the particle pull out from rubber matrix which indicates weak interaction between waste nickel zinc ferrite particles and rubber [11].

![SEM micrographs of fracture surface of rubber composites](image)

**Fig. 2.** SEM micrographs of fracture surface of rubber composites: (a) MRE without plasticizer and (b-f) MREs with different plasticizer contents of 5, 10, 20, 30, and 40 phr respectively

| Plasticizer content (phr) | Thickness (µm) | Length (µm) |
|---------------------------|---------------|-------------|
| 0                         | 2.5           | 39.2        |
| 5                         | 5.4           | 56.2        |
| 10                        | 6.2           | 149.8       |
| 20                        | 8.1           | 326.2       |
| 30                        | 10.6          | 614.1       |
| 40                        | 14.2          | 779.6       |

**Table 2.** Thickness and length of waste nickel zinc ferrite at different plasticizer content
3.3 Frequency Sweep

The variation of $\tan \delta$, $G'$ and $G''$ with frequency for MREs with different plasticizer contents is shown in Fig. 3. It can be seen that, $\tan \delta$ was increased with the increase of frequency until 20 Hz and subsequently decreased until 100 Hz. It can be also seen that the $\tan \delta$ appears to increase with increasing plasticizer content until it reached a maximum value at 5 phr and thereafter decreased at higher plasticizer contents (10, 20, 30, and 40 phr). The increase of $\tan \delta$ for MREs with 5 phr plasticizer was mainly due to increase in $G''$ as opposed to $G'$. The increase in $G''$ could be explained by the increased energy loss due to sliding of rubber molecular chains which would bring more viscous flow during deformation [13]. Furthermore, additional energy could potentially absorbed due to break down of interparticle magnetic interaction between neighbouring particles. At higher plasticizer content (from 10 to 40 phr), the decrease of $\tan \delta$ could be explained by decreasing stiffness of MREs. Decreasing stiffness might be due to the increase of space in the polymer chain. The plasticizer generally has bulky structures that provide polymers with more space to move around and prevent polymers from coming close together. Therefore, the plasticizer softening the polymers and reducing the elastic modulus [14].
3.4 Strain Amplitude Sweep

The variation of \( \tan \delta, G' \) and \( G'' \) with strain amplitude for MREs with different plasticizer contents is shown in Fig. 4. \( \tan \delta \) was amplitude dependent over the whole strain amplitude explored. MREs with 5 phr plasticizer had the highest \( \tan \delta \) with percentage increment of 17.63% in \( \tan \delta \) compared to MREs without plasticizer. It is apparent that the change in \( \tan \delta \) with increased strain amplitude is mainly due to the decrease in \( G' \). The amplitude dependence for MREs could be explained due to Payne effect. This effect could be related to the breakdown of filler aggregates to release trapped and occluded rubber which allows more rubber to take part in energy dissipation, filler rubber detachment and reformation that increases with increasing strain amplitude.

Furthermore, \( \tan \delta, G' \) and \( G'' \) for anisotropic MREs decreased with increasing plasticizer content. This is believed to occur due to poor filler-filler interaction in a bulkier chain like columnar structures and weak filler-rubber interaction. The weak filler-filler and filler-rubber interaction in anisotropic MREs can easily disrupted as the strain amplitude increased and therefore the magnetism induced damping reduced.
Fig. 4. Tan δ (a) storage modulus (b) and loss modulus (c) of MREs with different content of plasticizer with strain amplitude range of 0.1-6 %

4. Conclusion

Effect of plasticizer on the performance of MREs based on natural rubber and waste nickel zinc ferrite has been experimentally investigated. The addition of paraffin oil decreased the viscosity of polymer matrix due to reduction in cohesive attraction forces between polymer chains. SEM micrograph revealed that the waste nickel zinc ferrite particles organized into chain like columnar structure as a consequence of curing the material under an applied magnetic field at elevated temperature. Tan δ was found to be highest for the 5 phr plasticizer over the whole frequency and strain amplitude explored.

Acknowledgements

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