Effect of Petroleum-Based Oil Towards Physicochemical Properties of Natural Rubber-Based Magnetorheological Elastomers

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Abstract. This study presents an investigation of the effect of magnetorheological elastomers (MREs) using petroleum based-oil (PBO) as dispersing aids. The inhomogeneous dispersion and mobility of magnetic particles within the elastomer matrix result in poor MREs performance. Isotropic natural rubber (NR) based MREs were fabricated by homogeneously mixed with the addition of different ratios of naphthenic oil (NO) to aromatic oil (AO), whereby NO 1(100:0), NO 2 (70:30), NO 3 (50:50), and NO 4 (30:70), correspondingly. The cure characteristics, morphological, magnetic properties and thermal analyses were conducted. Based on the results, NO 1 leads the best results for microstructure observation and magnetic properties of the MREs. Meanwhile, NO 2 mixed with AO showed an improvement in curing characteristics and thermal analyses compared to other samples. In summary, the ratio of NO 1 and NO 2 is considered the preferable dispersing aids for MREs compared to NO 3 and NO 4 due to the structural compound in the oil that enhanced the characteristics of the NR-based MREs.

1. Introduction

A magnetorheological elastomer (MRE) belongs to smart material groups, which their rheological properties can be regulated continuously, reversely and rapidly controlled by an external magnetic field within an elastomer matrix [1]. These benefits provide a large variety of engineering fields in several applications including prosthetic devices, spring elements, automotive bushing, medical devices, and vibration absorbers [2-4]. MREs can be fabricated in two different states either isotropic and anisotropic which are known as with or without magnetic field is applied during the curing process, respectively. MRE is a composite material that consists of the main components such as matrix, magnetic particles and additives where all have shown great influences on the properties of MREs. The researchers found out that the selection of matrix for MREs is an essential part. Most MREs research groups used different types of rubber materials such as natural rubber (NR), silicone rubber (SiR) and polyurethane rubber (PU) as matrix [4]. In this study, NR was chosen as an alternative matrix. NR is a non-magnetic viscoelastic material and is well-known to exhibit an ideal matrix for excellent MREs performances, such as good dynamic performance, high elasticity and abundant availability [6].

Conventionally, dispersing aid such as silicone oil is used in the rubber processing for SiR to help the dispersion of filler and additive during that process. In this work, petroleum based-oil (PBO) was...
chosen as dispersing aid for unsaturated rubber matrix such as NR to enhance the rubber’s flexibility, reduce the viscosity of the matrix and improve processability [9]. The most commonly used PBO as dispersing aids is aromatic oil (AO) which has good compatibility with the rubber. The main characteristics of AO as dispersing aid such as good compatibility with the rubber and acts as a softening agent to improve the workability of rubber composition [7]. Based on these properties, AO may have the potential to improve the MR performance of MREs when mixed with other PBO [6]. Aziz et al. [5] have discovered other several oils which include epoxidized palm oil (EPO), petroleum based-oils (PBO) involving napthenic oil (NO) and light mineral oil (LMO) as additives for NR-based MREs. These oils showed a potential towards improving the dispersibility of magnetic particles within MREs performance. Based on their findings, the agglomeration of carbonyl iron particles (CIPs) still occurs in the MREs sample, where it causes a decrease of crosslink density and leads to poor MR performance. The mixture of NO:AO may reduce cohesive forces between polymer chains due to a high level of unsaturated rings and high reactivity with the rubber [6]. The characteristics of PBO have shown a significant effect on the process of rubber compounding and mechanical properties of the vulcanizate [8]. The addition of the proposed additives is expected to enhance the dispersion ability of the magnetic particles and consequently improves the MR performance [1,4,8]. Therefore, in this work, the evaluation of different ratios of NO:AO towards the performance of MRE are experimentally investigated and evaluated. NR-based MRE results in terms of cure characteristics, micrograph, thermal analysis, and magnetic properties were compared and discussed.

2. Research Method

2.1. Materials Preparation and Fabrication of MREs samples

The main components of MREs are elastomer matrix, magnetic particles and additives. Generally, the fabrication process of isotropic MREs consists of two stages: mixing and curing. Natural rubber (NR) was used as a matrix and prepared by the Malaysian Rubber Board. The CIPs were purchased from Sigma Aldrich, Germany and used as a magnetic particle in this study. The petroleum based-oil (PBO), which includes napthenic oil (NO) and aromatic oil (AO) were purchased by the Malaysian Rubber Board. Zinc oxide (ZnO) and stearic acid were used as an activator. Meanwhile, carbon black, sulphur and cyclohexyl benzothiazole-2-sulphenamide (CBS) were added as the function as reinforcing agents, crosslinking agent and accelerator, respectively. The schematic diagram of the fabrication process is shown in figure 1. The first stages of the mixing process were carried out using the conventional double-roll mill. The addition of ZnO, stearic acid, carbon black, NO and AO in the rubber. Then, sulphur and CBS were added and finally, the addition of CIPs was fixed at 60 wt%. Subsequently, the measurement of the curing time for isotropic MREs was determined using the Monsato Moving Die Rheometer (MDR 2000) at 150°C without the presence of a magnetic field. The final MREs compound was fabricated into 1.0 mm thickness. The ratios of NO to AO are shown in table 1 and the MREs samples were named as sample NO 1, NO 2, NO 3 and NO 4.

![Figure 1: A schematic diagram of the fabrication process of MREs](image-url)
Table 1: Compound ingredients for different ratios of NO to AO

| Sample | Ratio of PBO | Amount (phr) | Naphthenic oil | Aromatic oil |
|--------|--------------|--------------|----------------|--------------|
| NO 1   | 100:0        | 10           | 0              |              |
| NO 2   | 70:30        | 7            | 3              |              |
| NO 3   | 50:50        | 5            | 5              |              |
| NO 4   | 30:70        | 3            | 7              |              |

*Phr = parts per hundreds of rubbers

2.2. Characterizations of MRE samples

The cure characteristics were examined using a moving die rheometer (MDR) at a constant temperature of 150°C for 30 minutes. The parameters of cure characteristics were obtained such as cure time (t90) and scorch time (tS1). The vulcanization time of the MRE sample corresponds to the optimum cure time (t90) was calculated according to Equation (1).

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t_{90} = M_L + \frac{90}{100} (M_{H} - M_L)
\]

\(M_L\): Minimum torque value
\(M_{H}\): Maximum torque value

The morphology of the MRE samples was carried out through a Field Emission Scanning Electron Microscope (FESEM). The cross-section of samples was determined with a magnification of 500x at an accelerating voltage of 5kV during the experiment process. To prevent charging during the observation process, all samples were coated with gold. The magnetization curves of MR materials were measured at room temperature using a vibrating sample magnetometer (VSM). All the samples have been varied and were conducted under the magnetic field of -8000 to 8000 Oe. Thermal characteristics of the NR-based MREs were performed via thermogravimetric analysis (TGA) in a nitrogen atmosphere. The mass of each MREs sample was measured in the range of 8-10 mg based on standard sample preparation. The samples were heated at a temperature of approximately 25 to 800°C under a heating rate of 10°C/min.

3. Results and Discussion

3.1. Cure Characteristics

Figure 2 shows the cure curves of NR-based MREs with different ratios of NO:AO. The torque values increase with the increase of NO contents in NR-based MREs. It can be seen that reversion curing curves were acquired for the sample NO 1, NO 2, NO 3 and NO 4. Reversion curves occur at the final stage when some compounds are overheating during the test that corresponds to the breakdown of rubber networks. As compared to NO 1, NO 2 and NO 3, NO 4 shows the most reversion where torque decreases with time as shown in figure 2. This is probably due to the breakdown of the ring structure in oil between NR molecular chains.
The different ratios of NO:AO affects the cure characteristics of the NR-based MREs including the value of scorch time \( (t_{S1}) \) and the optimum cure time \( (t_{90}) \). According to table 2, NO 2 demonstrated the highest cure time in which the value is 3.79 minutes. This could be due to the addition of AO within the samples and consequently delay the curing process. Chandrasekara et al. [10], reported that NR compound containing AO has the highest cure time during the vulcanizing process due to the energy consumption as well as showed good processing safety.

**Table 2:** Cure characteristics of the NR-based MREs

| Sample | \( t_{S1} \) (min) | \( t_{90} \) (min) |
|--------|------------------|------------------|
| NO 1   | 3.42             | 8.64             |
| NO 2   | 3.41             | 8.79             |
| NO 3   | 3.43             | 8.75             |
| NO 4   | 3.49             | 8.54             |

3.2. Microstructure Observation

Figure 3 (a)-(d) shows the microstructure of isotropic MREs samples with different ratios of NO:AO. All MREs samples exhibit an isotropic condition and show a homogenous distribution of CIPs within the MREs. There were significant differences in the microstructure of MREs samples when AO was added with the NO. According to figure 3 (a), a small agglomeration is observed in MREs sample containing NO without mixing with AO and the void still occurs in the sample. It can be seen that CIPs can blend well with the matrix and dispersing aids. This is due to the high content of NO that is compatibility with NR and more stable as compared to AO. Meanwhile, in Figure 3 (b), (c) and (d), the MREs samples formed large aggregations and void in the presence of more AO. The unsaturated rings in the AO could be the reason for the large agglomerations that occurred.
3.3. Magnetic Properties

Figure 4 illustrates the magnetization curves of NR-based MREs with different ratio of NO:AO, while table 3 presents the magnetic parameters that had been obtained from figure 4. Based on the magnetization curves shown in figure 4, the saturation magnetization of NO 1 has the highest magnetization curves. It could be due to the high content of NO which the particles homogeneously dispersed in the samples. Hence, the NO 1 has high compatibility with the rubber as compared to the NO 2, NO 3 and NO 4. The magnetization curves of NO 3 showed the lowest in figure 4. This is referred to the movement of the particles, where the ratio of NO:AO is 50:50 had reached saturation magnetization easily. Besides, the saturation magnetization value for NO 3 was insignificant with the NO 4.

Table 3 represents the saturation magnetization ($M_s$), retentivity magnetization ($M_r$) and coercivity ($H_c$) at different ratio of PBO in which the values are obtained from figure 4. It can be seen that the rise of NO content contributes to the enhancement of magnetic properties of the NR-based MREs. This is proven by the increasing of $M_s$ with NO content as referred in table 3. The NO 1 showed the highest magnetic saturation and followed by NO 2, NO 4 and NO 3 with 40.06, 28.73, 18.74 and 17.23 emu/g, respectively. The compatibility and interaction between matrix and filler are the predominant factors in
improving the performance of MREs. By using the different ratio of NO:AO, the magnetic properties had significantly changed. It can be seen the MREs with NO 1 has the highest magnetic saturation as stated in table 3.

| Samples | $M_s$ (emu/g) | $M_r$ (emu/g) | $H_c$ (Oe) |
|---------|--------------|---------------|------------|
| NO 1    | 40.06        | 0.18          | 16.38      |
| NO 2    | 28.73        | 0.13          | 15.57      |
| NO 3    | 17.23        | 0.075         | 16.77      |
| NO 4    | 18.74        | 0.078         | 16.36      |

3.4. Thermal Characteristics

The thermal stability of a polymer can be evaluated by using TGA. The effect of NR-based MREs with different ratio of NO:AO was measured using thermogravimetric analysis in a nitrogen atmosphere are demonstrated in figure 5. The thermal decomposition of MREs samples consists of two types which are known as the first stage and second stage shown in figure 5. The first stage of thermal decomposition begins at a temperature between 260 to 343°C while the second stage occurred at 315 to 465°C. The initial decomposition of all the samples occurred during the first stage. Afterwards, TG patterns were dramatic decrease during the second stage. According to figure 5, NO 1 and NO 4 showed higher weight loss as compared to other samples. This is due to the presence of different ring structure in oil. The NO consists of a saturated ring structure while AO has an unsaturated ring structure. These rings were reacted with CIPs via a chemical reaction and consequently cause the corrosion occurred and affect the CIPs in the MREs samples at the high temperature. In addition, the presence in the matrix of different structural NO and AO rings could occupy the space between the rubber chains. However, due to the labile structures in the rubber chains, the material easily decomposed at low temperatures decreases so that it breaks easily.

![Figure 5: TGA curves of NR-based MREs with different ratio of NO:AO](image)

The degradation temperature of MREs with different ratios of NO:AO obtained from thermograms are summarized in table 4. $T_{\text{onset}}$ represents the temperature at which the NR matrix begins to degrade while the $T_{\text{end}}$ corresponds to the end of degradation. It can be seen that the $T_{\text{onset}}$ for NO 1 is lower than the other samples as shown in table 4. $T_{\text{onset}}$ from NO 1 to NO 2 increased from 260 to 300°C and then decreased from 290 to 280°C with an increase in AO content. High NO content has delayed degradation.
The effect of NO on the thermal decomposition of MREs could be due to the presence of a saturated ring which delays the degradation of the MREs. The saturated ring structure in the oil may take longer to break down the rubber chains. The addition of dispersing aids could occupy the space between the rubber chains. Other than that, it assumes that the different ratios of NO to AO, have had a significant impact on the characteristic NR temperature and weight loss.

**Table 4:** Thermal degradation temperature of MREs with different ratios of NO:AO

| Samples  | T_onset(°C) | T_end(°C) | Ash at 800°C (%) |
|----------|-------------|-----------|------------------|
| NO 1     | 260         | 450       | 10               |
| NO 2     | 300         | 465       | 30               |
| NO 3     | 290         | 457       | 26               |
| NO 4     | 280         | 454       | 8                |

**4. Conclusion**

In this work, the influences of different ratios of NO to AO as dispersing aids with 60 wt% CIPs on the performance of isotropic NR-based MREs was investigated. The results revealed that scorch time decrease and optimum time increased for the NO 2. The results of morphology revealed the formation of CIPs in an isotropic state. The addition of PBO as dispersing aids allowed the molecular chains of rubber to glide easily and consequently reduce the gap and agglomeration of magnetic particles. The NO showed an improvement in morphology observation and magnetic properties due to the stronger bonding of NR and CIPs which favorable for MREs applications since MREs are exposed to various magnetic field strength. Sample NO 1 has indicated the best ratio for morphology observation and magnetic properties. In a nutshell, NO has a great influence on MRE properties of NR-based MREs due to the good compatibility between rubber and oil and could be a promising material for certain MRE applications. Studied mechanical properties such as tensile properties and damping performance could be considered for future work particularly for implementation of MRE in automotive and civil industries.

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