DEVELOPMENT OF MAGNETORHEOLOGICAL ELASTOMERS BASED ON NATURAL RUBBER AND INDUSTRIAL WASTE NICKEL ZINC FERRITE

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DEVELOPMENT OF MAGNETORHEOLOGICAL ELASTOMERS BASED ON NATURAL RUBBER AND INDUSTRIAL WASTE NICKEL ZINC FERRITE

by

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LIST OF SYMBOLS

Hz	Hertz
µm	Micrometer
%	Percent
wt%	Weight percentage
dNm	Desinewtonmeter
min	Minute
MPa	Megapascal
°C	Degree celcius
M_H	Maximum torque
M_L	Minimum torque
phr	Part per hundred rubber
mm	Millimetre
g	Gram
t_{s2}	Scorch time
t_{90}	Cure time
mT	Millitesla
V_0	Molar volume of toluene
V_p	Volume fraction of the particles

V_r	Volume fraction of MREs
ρ_r	Density of natural rubber
ρ_s	Density of toluene
X	Interaction parameter between rubber and toluene
m_{dry}	Dry mass of MREs
m_{wet}	Swollen equilibrium mass
cm^{-1}	Per centimeter
kg/m^3	Kilogram per cubic metre
cm^3/mol	Cubic centimeter per mole
kV	Kilo volt
G'	Storage modulus
G"	Loss modulus
$\tan \delta$	Tan delta
M_1	Original mass of MREs rubber
M_2	MREs rubber swollen mass
M_s	Saturation magnetization
M_r	Remanence
H_c	Coercive force

LIST OF ABBREVIATIONS

APTES	(3-aminopropyl) triethoxy silane
ASTM	American Society of Testing and Materials
BR	Butadiene rubber
CBS	N-cyclohexyl-2-benzothyazolsulfenamide
DPG	Diphenyl guanidine
EP	Epoxy resin
FTIR	Fourier Transform Infrared Spectroscopy
IPPD	N-isopropyl-n'-phenyl-p-phenylenediamine
ISO	International Standards Organisations
MBT	Mercaptobenzothiazole
MR	Magnetorheological
MREs	Magnetorheological elastomers
MRFs	Magnetorheological fluids
PANI	Polyaniline
phr	Parts per hundred rubber
PU	Polyurethane
SBR	Styrene Butadiene Rubber
SEM	Scanning Electron Microscope

SMR	Standard Malaysian Rubber
TESPT	Bis [3-(triehoxysilyl) propyl] tetrasulfide
TGA	Thermal gravimetric analysis
TMTD	Tetra-methylthiuram disulphide
TSR	Technically Specified Rubber
ZDBC	Zinc dibutyl dithiocarbamate
DOP	Diisooctyl phthalate

PENGHASILAN ELASTOMER MAGNETOREOLOGI BERDASARKAN GETAH ASLI DAN SISA INDUSTRI NIKEL ZINK FERIT

ABSTRAK

Elastomer magnetoreologi (MREs) yang terdiri daripada getah dan zarah magnet mendapat peningkatan perhatian dalam aplikasi kejuruteraan dan penyelidikan kerana prestasi cemerlangnya dalam sifat dinamik. Dalam penyelidikan ini, MREs berasaskan sisa industri nikel zink ferit dan getah asli telah dihasilkan. Ciri-ciri dinamik dikaji menggunakan nilai tangen yang hilang, tan δ. Ciri-ciri vulkanisasi, kestabilan haba, ciri-ciri morfologi juga dinilai dalam kerja ini. Bukti daripada SEM menunjukkan MRE isotropik telah didapati mempunyai pembahagian zarah yang seragam manakala MRE anisotropik mempunyai susunan zarah magnet. Walau bagaimanapun, jarak nyata antara nikel zink ferit dan getah asli adalah lemah. Tan δ bagi MRE anistropik adalah tinggi berbanding MRE isotropik untuk seluruh julat kekerapan and amplitud ketegangan yang dikaji. Peningkatan gandingan antara nikel zink ferit dan getah asli dilaksanakan melalui penggunaan bis [3- (triehoxysilyl) propil] tetrasulfida (TESPT) sebagai rawatan permukaan zarah magnet dengan nilai 2, 4, 6, 8, dan 10% berat. Hasil kajian menunjukkan silana pengkupalan meningkatkan kekuatan mekanikal dinamik dan kekuatan tensil dan kandungan optimum TESPT adalah 6% berat. Tan δ daripada MREs yang dinaik taraf mengandungi tambahan karbon hitam juga dibandingkan dengan getah redaman konventional. Hasil kajian menunjukkan bahawa tan δ MREs yang dinaik taraf adalah lebih tinggi daripada

sampel perbandingan yang menyokong nikel zink ferit mampu meningkatkan sifat dinamik.

DEVELOPMENT OF MAGNETORHEOLOGICAL ELASTOMERS BASED ON NATURAL RUBBER AND INDUSTRIAL WASTE NICKEL ZINC FERRITE

ABSTRACT

Magnetorheological elastomers (MREs) which consist of rubber and magnetic particles have attracted increasing attention in engineering applications and research due to its excellent dynamic performance. In this work, MREs based on industrial waste nickel zinc ferrite and natural rubber was produced. The dynamic properties were investigated using lost tangent, tan δ. Curing characteristics, thermal stability, morphology characteristics were also evaluated in this work. From SEM results, it was evident that isotropic MRE has uniform magnetic fillers dispersion in rubber matrix while anisotropic MRE had chain like structure of magnetic filler, however, the interface between nickel zinc ferrite and rubber matrix was poor. Tan δ for anisotropic MREs were found higher compared with isotropic MREs over the whole range of frequency and strain amplitude explored. The adhesion between nickel zinc ferrite with natural rubber matrix was then improved by using bis [3-(triehoxysilyl) propyl] tetrasulfide (TESPT) as the surface modification for magnetic particles with varied content at 2, 4, 6, 8, and 10 wt%. The result revealed that silane coupled improved the dynamic mechanical strength and tensile strength and the optimum content of TESPT was 6 wt%. Tan δ of developed MREs with addition of carbon black also were compared with conventional damping rubbers. The results revealed that tan δ was higher than comparative samples supporting the nickel zinc ferrite to improve dynamic properties.

CHAPTER ONE

INTRODUCTION

1.1 Background of study

Rubber is a unique material which it offers both elastic and viscous properties. Being a viscoelastic material, rubber is by far the most selected material to be used in vibration damping. Although rubber has the capability to absorb vibration, some of the drawbacks of rubber such as low stiffness has limit its application in enormous field of applications. In order to overcome the drawbacks, researchers had found that rubber incorporated with metallic or ceramic particles exhibits potential improvement in mechanical performance while maintaining the damping performance (Wang et al., 2011, Makled et al., 2005). Further improvement of rubber has been found to introduce magnetic particles in rubber which resulting better damping and structural performance. Generally, rubber matrix with addition of magnetic particles are called as magnetorheological elastomers (MREs) or magnetoelastomeric rubber (Stepanov et al., 2007).

There are several advantages of MREs when compared with basic rubbers. As the matrix used for MREs are from rubber, the performance of the MREs mainly influenced by the viscoelastic properties of the rubber matrix itself, same does with basic rubber. However, incorporation of magnetic particles in MREs provide special reinforcement effect which is through the magnetic particles interaction and interfacial friction between the particles and rubber matrix. Furthermore, the stiffness and dynamic mechanical properties of the MREs can be varied by application of an applied magnetic field during fabrication or in service. MREs are the improved generation of magnetorheological (MR) materials following on from magnetorheological fluid

(MRF), in which the matrix used is from a solid elastomeric material rather than carrier oil. The idea to replace oil with rubber matrix successfully solved the particle sedimentation problem in MRF and obvious advantage from that idea is no containers or seals is needed to hold the fluid and also can prevent leakage. MREs are being used in various applications such as adaptive tuned vibration absorbers (Deng and Gong, 2008), auto-motive engine mounts (Ginder et al., 1999), and semi active seismic dampers (Dyke et al., 1996).

Generally, MREs can be fabricated into two types, which are 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 during curing under an elevated temperature. The influence of magnetic field caused the individual magnetic particles to attract different pole of one each other resulting the formation of chain-like structures and upon curing, the magnetic particles are set in place inside the matrix. These chain like structure of magnetic particles was found to provide much larger damping and stiffness values.

1.2 Problem statement

Dynamic mechanical performance of MREs is considered to be ascribed to viscoelastic behaviour of the rubber matrix, interfacial damping at the interface between the magnetic particles and the matrix and also magnetism induced damping. It is apparent that the main factors to fabricate MREs are selection of rubber matrix and the magnetic particles. Recently, numerous works have been carried out to investigate the dynamic mechanical properties of MREs with various kinds of magnetic particles. Most of the researches use carbonyl iron as their chosen magnetic particles. The use of carbonyl iron in MREs was extensively explored. Jung et al. (2016) conducted an experiment to compare the performance of natural rubber MREs incorporated with carbonyl iron. Aloui and Klüppel (2014) reported on hybrid magnetic fillers of carbonyl iron with nano-particles MagSilica. An investigation on bimodal particle based on different size of carbonyl iron also has been reported by Li and Zhang (2010). Shuib et al. (2015) explore the use of iron sand in MREs, however the wider size distribution of iron sand particles influences the processability of MREs. These magnetic particles used in the previous literature are high cost and cheaper particles do not perform very well. Low cost products with high performance are desirable in current development direction.

In this development era, industrial production increases and of course the amount of waste generated also increases. In order to prevent landfill and negative impact on environment, the use of waste materials seem promising. It is observed that none of the literature investigate the performance and possibility of waste magnetic particles which contain heavy metal that can lead to soil and water pollution to be incorporated in MREs. The waste magnetic particles are being inexpensive and highly available. The incorporation of waste magnetic particles in MREs is an attractive approach from the view point of profit earning, recycling and sustainable environment.

In this study, industrial waste nickel zinc ferrite was chosen as the magnetic particles added in natural rubber to produce MREs. Nickel zinc ferrite has high permeability and saturation magnetisation, low cost, and smaller size distributions. It is derived from electronic manufacturing waste which is abandoned regardless of the large amount of ferrite (as high as 70% in nickel-zinc ferrite waste) and cannot be recycled due to impurities and very complicated composition. Furthermore, the waste contains heavy metal elements which could cause dangerous effect to human health and environment if it is not treated properly prior to disposal (Sezgin et al., 2013).

Development of MREs based on industrial waste nickel zinc ferrite and natural rubber in this work is a novel direction. Indeed, to date, none of the research work has been done using industrial waste as magnetic particles in MREs. One of the limitations of using waste nickel zinc ferrite in rubber matrix is the incompatibility and level of adhesion between the particles and rubber matrix in which the interaction of particles and rubber matrix should be sufficiently strong to obtain efficient stress transfer from the matrix to the magnetic fillers. This sets a challenge in MREs as the inorganic magnetic fillers are inherently incompatible with organic rubber matrix which leads to poor wettability and adhesion between the filler and matrix. Therefore, surface modification of nickel zinc ferrite magnetic fillers is an attractive approach in order to promote adhesion and enhance the dispersion of magnetic fillers within the rubber matrix to successfully produce high performance final product.

Surface modification of inorganic particles nickel zinc ferrite in this research was achieved by bifunctional coupling agent treatment using silane based coupling agents which is the most successful and cost effective treatment. These chemicals are silicon-based chemicals that contain hydrolysable groups (such as methoxy, ethoxy or acetoxy) at one end that will interact with inorganic materials and organofunctional groups (such as amino, vinyl or sulphide) at the other end that can react with the rubber matrix. Therefore, inorganic and organic materials can be coupled together with the silane coupling agent acting as a bridge between them to improve compatibility and interfacial interaction of MREs.

1.3 Research objectives

The main focus of this research was to fabricate isotropic and anisotropic MREs based on industrial waste nickel zinc ferrite and natural rubber that have good dynamic properties for potential use in vibration damping applications. The specific objectives in this research are listed as follows:

- To fabricate MREs based on industrial waste nickel zinc ferrite and natural rubber and to evaluate the microstructure (isotropic and anisotropic), curing characteristics, thermal stability, dynamic, mechanical performance of MREs and to select the best formulation.
- To assess the effect of surface modification of nickel zinc ferrite for improving the adhesion between nickel zinc ferrite and rubber matrix and to evaluate its influence on curing characteristics, thermal stability, mechanical and dynamic mechanical properties of isotropic and selected anisotropic MREs containing nickel zinc ferrite.
- To characterize and compare the dynamic and mechanical performance of selected MREs based on industrial waste nickel zinc ferrite and natural rubber with conventional antivibrations rubber.

1.4 Outline of the thesis

This thesis is organized into five chapters. Each chapters cover the research interest as mentioned under the research objectives section:

Chapter 1: Introduction of Magnetorheological Elastomers in general, previous research works regarding MREs, objectives and problems statement.

Chapter 2: Provide the literature review related to MRE and extensive review of material used in this research including chemical used in surface modification of waste nickel zinc ferrite.

Chapter 3: Precisely describe the experimental procedure involved in the preparation of MREs based on industrial waste nickel zinc ferrite. Provides summary of materials and chemicals, as well as machine and testing procedure used in this research including the specification and variables used are explained in details.

Chapter 4: Data and results obtained from the research according to the objectives are discussed and be presented in details.

Chapter 5: Summary and conclusions on this present work as well as suggestions for the further research work.

CHAPTER TWO

LITERATURE REVIEW

2.1 Magnetorheological materials

Magnetorheological (MR) materials is one of the new materials for engineering application. The advantage of MR materials is the rheological properties can be changed rapidly under an applied magnetic field. These materials are being developed to improve the performance of rubber as a commonly used material for dynamic applications. Generally, MR materials are produced by two constituent materials which are non-magnetic medium (normally an oil or elastomer) and magnetic permeable particles. The performance of these materials mainly promote by the viscoelastic properties of the non-magnetic medium, but inclusion of magnetic particles enables additional reinforcement through magnetic particles interaction and interfacial friction between the particles and non-magnetic medium. The development of MR materials started from the first patent by Jacob Rabinow in 1940s (Rabinow, 1948). MR materials can be classifies into MR fluids (MRFs), and MR elastomers (MREs). The details characteristics of MRFs and MREs are discussed in the following section.

2.1.1 Magnetorheological fluids (MRFs)

MRFs are one of the MR materials which consist of magnetisable filler dispersed in a fluid (commonly oils). The MRFs change instantaneously for about milliseconds from a liquid state (Newtonian behaviour) to semi solid state (viscoelastic) with a certain value of yield stress under magnetic field (Chen and Liao, 2010). During the exposition of MRFs to a magnetic field, the materials changes to that more of a solid due to the magnetization of the magnetisable particles which influenced by magnetic fields to structure following the direction of the external magnetic fields resulting the restriction of fluid to flow (Carlson and Jolly, 2000). Figure 2.1 shows illustration of magnetic particles structure in MRF without magnetic field and with magnetic field.

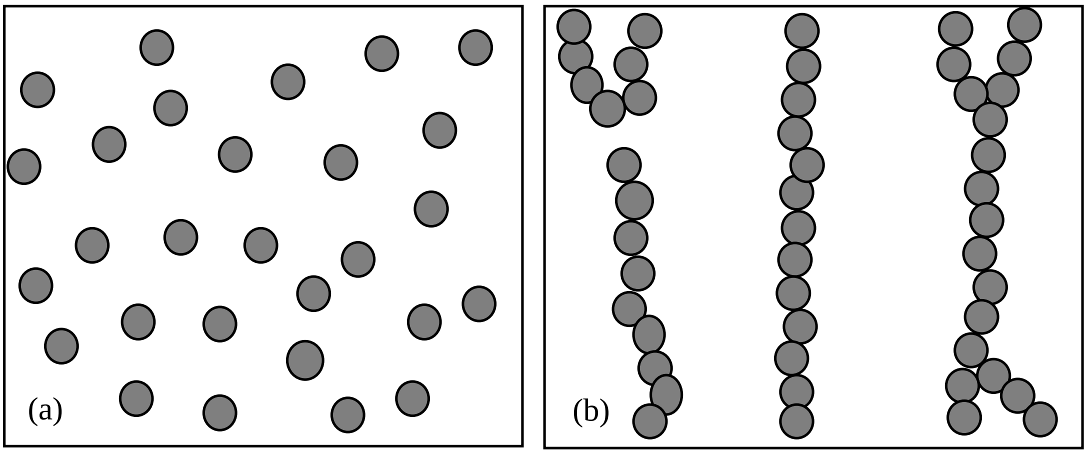


Figure 2.1 MRF structure; (a) without magnetic field and (b) with magnetic field

The increase of magnetic field applied to the carrier matrix will influence more magnetisable particles to form chain structures and consequently, more yield strength is developed within the fluid. These cluster of chains and columns increase the strength of MRFs, however, extra force exerted on the MRFs may disrupt the structure and lead to deformation (Carlson and Jolly, 2000, Kciuk and Turczyn, 2006).

MRFs have gained attentions due to its fast response and easy preparation procedure. It is widely used in many applications, such as vibration suppression of mechanical components, shock absorbers, rotary brakes, clutches and artificial knees (Spaggiari, 2013). However, the MRFs sedimentation caused by particles mismatch density with carrier fluid remains a major issue which may negatively affect the performance and increase its risk of failure.

2.1.2 Magnetorheological elastomers (MREs)

MREs have drawn a lot of attentions nowadays after MRFs. Generally, MREs is a similar material like MRFs, but the matrix used is a solid elastic polymer instead of carrier oil. MREs is more preferable because it can overcome the shortcoming exposed by MRFs which is particle sedimentation. Moreover, solid elastic polymer in MREs are easily handled and easy to process.

The stage of choosing materials is very important to produce high performance of MREs. The most commonly matrix materials used for MREs are natural rubber, epoxidized natural rubber, polyurethane rubber, silicone rubber or cis-polybutadiene rubber while iron is the most used particles. Iron has high permeability, low remnant magnetisation, and high saturation magnetization (Lokander and Stenberg, 2003). High permeability and saturation magnetisation provide high interparticle attraction, and thereby produce stronger chains and columnar structures.

MREs are generally operate within the pre-yield region, because the rubber matrix does not yield. Unlike MRFs, which typically work in post-yield region. In the pre-yield region, a material behaves like a linear viscoelastic material, while in the post-yield region flow occurs. The difference of working modes between MREs and MRFs influence the performance of these two MR materials which is the MREs exhibits higher stiffness and dynamic mechanical performance compared to MRFs (Li et al., 2013)

MREs can be characterized into isotropic and anisotropic. A uniform magnetic particles distributed in matrix material can be observed for isotropic MREs Anisotropic MREs have alignment of magnetic particles in the rubber due to curing the matrix under an external magnetic field. During curing process, magnetic force influence magnetic particles to attract head-to-tail (the north pole of one particle to attract the south pole of its neighbour) parallel to the field direction, thus forming chain like structure inside the matrix and locked upon curing. Anisotropic MREs are found to produce material with much larger stiffness and damping compared to isotropic MREs.

2.1.3 MREs applications and challenges

MREs based devices play wide role in engineering scope: mechanical and civil engineering. Commonly, the MRE-based devices are used for vibration control in damping and isolation systems. For automotive applications, MREs are applied in the vibration absorber system to reduce vibration comes from engines, motor, and pumps during rotational imbalances. Furthermore, MREs also used to reduce shudder produced from dissatisfaction breaking events. The Ford Motor Company has produced an automotive bushing from MREs (Ginder et al., 1999). By verifying the magnetic field of MREs devices, the dynamic stiffness can be adjusted, thus, vibration and noise produced from vehicle system can be controlled.

In civil engineering field, MREs devices are widely used in prevention method to avoid structures from earthquake damage (Ni et al., 2010). A new semi-active MRE isolator was developed with a concept of transition between traditional passive isolators and active isolators (Behrooz et al., 2014). The semi-active MRE isolator consists of traditional steel–rubber vibration absorber, as the passive element, and MREs with a controllable stiffness and damping behaviour, as the semi-active elements. This development is a fail-safe design to guard structure against a wide range frequency of earthquake and it is being used in civil isolation structure system. Furthermore, MREs also used for sensor applications. Few researchers have explored the possibility to develop MRE based sensing device. Bica (2011) has experimentally investigated on the magnetoresistor sensor designed by using graphite MRE to detect the magnetic field. Recently, stretchable, compressible and magneto-sensitive strain sensor based on conductive MRE was designed. The MRE sensors can be integrated on a shoe to detect the foot motion (Hu et al., 2018).

MREs are being explored to be used for various applications and the development of MREs become the driving force for a better future technology. However, the most crucial issue arises from developing MREs for commercializing is the cost. The employment of iron in MRE devices invest a lot of money. Despite of quality and performance of MREs, the cost of these materials could be reduced by minimizing the use of iron in the fabrication process of MREs. Furthermore, the particles embedded in the matrix have a magnetic saturation point which limit the performance of MREs once it reached the point. Overcoming limitations of MREs will lead for a better improvement and rising of new applications.

2.2 MREs components

2.2.1 Rubber matrix

The selection of suitable matrix materials for MREs are crucial because it mainly influence the performance of MREs. The materials used for MREs matrix are commonly has non-magnetic properties which helps magnetic filler to easily dispersed within it. Typically, the selection of matrix materials is based on the viscosity of the materials which to consider the ability of the matrix to allow the magnetic particles to move and organize during process, particularly for anisotropic MREs (Boczkowska and Awietjan, 2012). In addition, the matrix also must be easy to process and has low permeability which can help to avoid any interaction between matrix and particles from occur, and consequently minimize the interaction between neighbouring particles. There are two types of matrix materials commonly used in MREs which are saturated elastomers and unsaturated elastomers. The unsaturated elastomer cured by sulphur vulcanization, differ from saturated polymer which generally does not need sulphur in the curing process. Table 2.1 shows the commonly used matrix materials for MREs.

Table 2.1 Matrix materials used in MREs

Matrix type	**Reference**
Natural rubber	An et al. (2017), Jung et al. (2016), Yoon et al. (2013), Lin et al. (2013), Chen et al. (2007)
Silicone rubber	Pössinger et al. (2013), Wang et al. (2007), Nayak et al. (2015)
Polybutadiene rubber	Sun et al. (2008), Fuchs et al. (2007)
Polyurethane rubber	Yu et al. (2017)
Ethylene propylene diene rubber	Wang et al. (2016)

As shown in Table 2.1, silicone rubber and natural rubber seems to be most attracted matrix materials used in research studies. Silicone rubber is one of the saturated elastomer which is easily fabricated because it is physically in a liquid state in the preliminary step. In addition, it is also well known as soft elastomer matrix due to its low viscosity which allows magnetic particles to easily move and uniformly dispersed within it (Puente-Córdova et al., 2018). Furthermore, silicone rubber also good in prevent oxidation attack (Rahimi and Mashak, 2013). Silicone rubber also has unique properties which it is easily fabricated and can form crosslinks in room temperature. But, silicone rubber has its disadvantages such as shorter fatigue life and low strength, which is it turns out to be not the most preferable matrix to be used in some applications. The drawback exposed by the silicone rubber then restrict the scope of its applications.

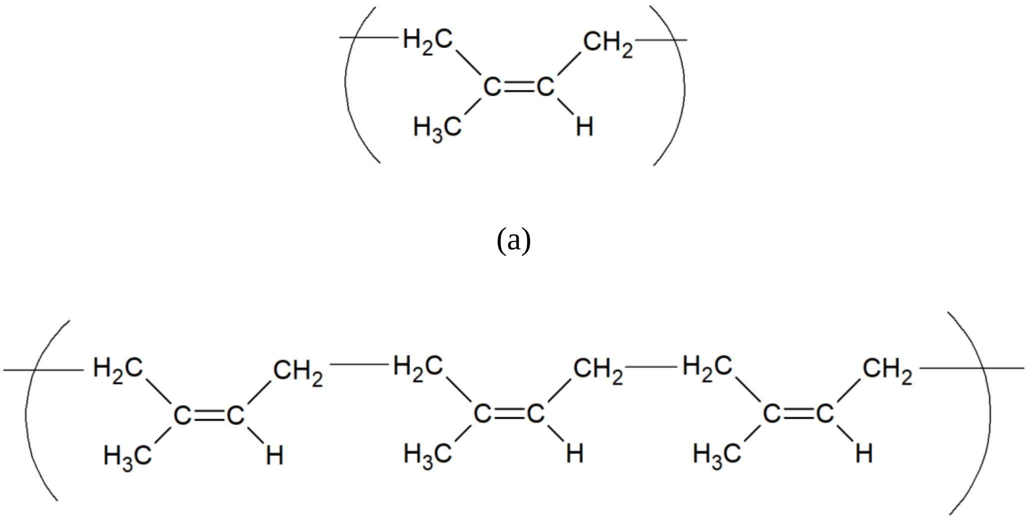
Unsaturated rubber, which is natural rubber received the most interest in MREs. The use of natural rubber matrix for MREs generally perform better than silicone rubber and any other matrices. It is good in mechanical properties and dynamic performance. As evidence, the tensile and tear strength of natural rubber based MREs are approximately 90% higher than MREs based on silicone rubber (Chen et al., 2007). In addition, the tan δ of natural rubber based MREs also shows higher value than MREs based on silicone rubber (Blom and Kari, 2005). Therefore, natural rubber possibly can be the suitable matrix for MREs and could be used in most applications such as vibration absorbers, rubber mounting and rubber bushing.

2.2.1(a) Natural rubber

Natural rubber is a high molecular weight polymer in a milky sap form found in the bark of tropical tree named Haveabraziliensis. It is a linear polymer and built up from repeated units of cis-polyisoprene chains (Figure 2.2). Haveabraziliensis also contains non-isoprene components such as proteins, carbohydrates, lipids and inorganic substances which also play an important role in controlling the inconsistency of its quality to produce excellent properties of natural rubber. Table 2.2 shows an analysis of natural rubber composition.

Table 2.2 A typical composition of natural rubber (Vaysse et al., 2012)

Constituents	**Percent w/w dry matter**
Rubber hydrocarbon	94.0
Proteins	2.2
Carbohydrates	0.4
Lipids	3.4
Organic solutes	0.1
Inorganic substances	0.2



(a)

(b)

Figure 2.2 (a) cis-polyisoprene, (b) linear chain structure of cis-polyisoprene (Eng et al., 1992)

Production of the natural rubber begins with tapping the sap from rubber tree until these material is then baled and shipped off to the rubber processor. Generally, after tapping, the sap from the rubber tree is added with ammonia solution and undergoes continuous centrifugation to produce sap concentrate (latex) for manufacturing products such as gloves and condoms. It can be also coagulated into baled rubber and shipped off to the rubber processor to produce bulk rubber products. The classification for baled rubber are reported in Technically Specified Rubbers (TSR) scheme. This standard was first developed for Standard Malaysian Rubber (SMR), but currently it is being adopted by other rubber producing country (Comyn, 1997). These rubbers are characterized based on dirt, ash, nitrogen and volatile substances content. Table 2.3 shows standard raw rubber values of SMR.

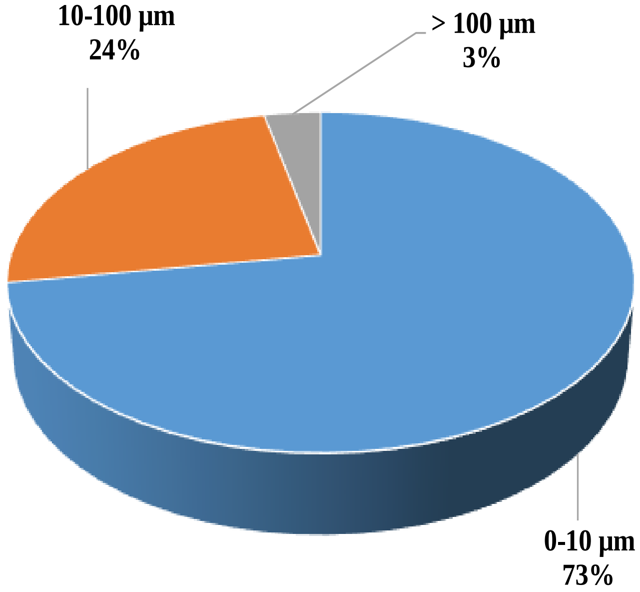
Table 2.3 Standard raw rubber value of SMR

Properties	**SMR 10**	**SMR 20**	**SMR L**	**SMR CV 60**
Dirt content, max, %	0.065	0.104	0.005	0.010
Ash content, max, %	0.37	0.50	0.28	0.35
Volatile matter, max, %	0.36	0.39	0.32	0.23
Nitrogen content, max, %	0.32	0.39	0.50	0.47
Initial Wallace plasticity P0, max	49.0	41.0	51.0	32.0
Plasticity retention index, max	82	83	96	91

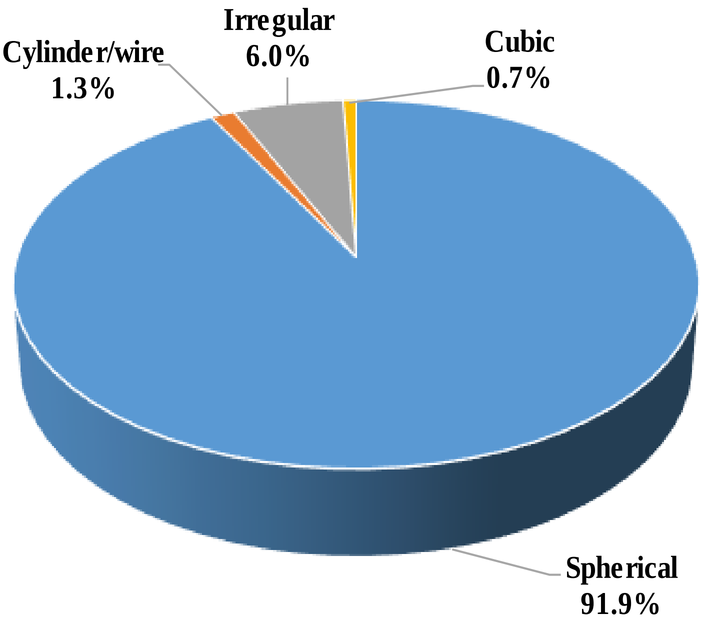
The major advantage of natural rubber is its crystallization properties. The strength of natural rubber is undoubtedly even in pure condition and it also exhibit highest failure elastic strain compared to any rubber. Manufacturer commonly compound natural rubber with chemicals and additives to produce rubber product. A rising field for natural rubber product is mostly in engineering application as it has an unbeatable performance in dynamic properties. It has high damping capability over the range of 1 to 200 Hz (Ciesielski, 1999). As such, it is used in rubber bearing, antivibration rubber, engine mount and vibration isolator.

2.2.2 Magnetic particles

The magnetic particles chosen for MREs are commonly have high magnetic permeability and high saturation magnetization. The high dynamic performance of MREs are as a result of strong inter-particle interactions between neighbouring particles that can be achieved by high permeability and saturation magnetization of the particles. These magnetic particles can align to produce longer and bulkier chains and columnar structure under high application of magnetic field. In the selection of magnetic particles for MREs, the size of the magnetic particles should be considered carefully because its influence the MREs performance in maintaining several magnetic domains. Figure 2.3 shows percentage of particle size and shapes of some of the commonly used particles in MREs.



(a)



(b)

Figure 2.3 Mapping of MREs based on magnetizable particle; (a) based on particle size, (b) based on particle shape (Sutrisno et al., 2015)

As can be seen in Figure 2.3(a), the most preferred size range is below 10µm, which is about 72.5%. The particle size of 10-100µm shows interest of 24.2% while above 100µm is 3.4%, respectively. A lot of research on the particle size of magnetic particles for MREs has been explored. Kumar et al. (2018) have proven experimentally that particle size has an influence on the response force of magnetic field and mechanical performance of MREs, however dynamic performance was not reported. In their work, MREs with different size of carbonyl iron particles ranging from 3-5 µm (small size) and 6-11µm (large size) were produced. It was found that the smaller carbonyl iron particles can move faster when applying the magnetic field than the larger carbonyl iron particles, and the carbonyl iron particles distribution increase the compressive modulus and response behaviour.

The investigation on the effect of particle size on interfacial friction damping properties also has been studied. In the research, the magnetic particles are varied with sizes of 1.1µm and 9.0µm. The results indicated that the dynamic performance including shear storage modulus and loss factor for MREs fabricated with 1.1µm tend to reduce when compared to MREs contained 9.0µm because the smaller particles tend to form agglomeration (Fan et al., 2011).

Figure 2.3(b) shows the percentage of different particle shapes filler used in research interest of MREs. Spherical shaped magnetic particles showed the highest interest which is about 91.9%, then irregular shape with 6.0%, cylinder shape with 1.3 % and the lowest is cubic shape with 0.7%. The spherical shape magnetic particles are widely commercialized and it gained most interest due to it can move easily during mixing and pre-curing process, especially in viscous-liquid based MRE.

Table 2.4 List of particle types commonly used in MREs

Particle type	References
Carbonyl iron	An et al. (2017), Chen et al. (2016), Jung et al. (2016), Małecki et al. (2016), Qiao et al. (2012)
Pure iron	Chokkalingam et al. (2011), Lokander and Stenberg (2003), Kaleta et al. (2011)
Iron oxide	Zhou et al. (2011)
Barium ferrite	Makled et al. (2005)
Strontium ferrite	Tian et al. (2013)

Table 2.4 shows the list of commonly particle types used in MREs. In current literature, carbonyl iron and pure iron are the most preferable used magnetic particles in MREs, however these particles are high in cost. Therefore, in this study, waste nickel zinc ferrite was chosen as the new alternative substitution for these high cost magnetic particles. Since waste nickel zinc ferrite magnetic particles is a waste magnetic filler, being inexpensive, and highly available, nickel zinc ferrite particles have added values to be an interesting magnetic filler source for MREs. It is discussed further in following section.

2.2.2(a) Waste nickel zinc ferrite

Nickel zinc ferrite is one of the ceramic ferro magnetic materials which contains a mixture of Nickel and Zinc metallic cations with chemical formula of $Ni_{1-x}Zn_xFe_2O_4$. Nickel zinc ferrite is an inorganic material with spinel structure. These material has high permeability and saturation magnetization as well as low magnetic coercivity (Song, 2011). It is also well known being extensively used in broad range of applications such as in manufacturing of electronic inductors, core material for power transformers in electronics, antennas and devices that are applied in the communication, lighting, alternative energy and automotive (Song, 2011). The secondary raw materials from the manufacturing which is one of the heavy metal elements are abandoned regardless of the large amount of ferrite (as high as 70% in nickel zinc ferrite waste) without recycling because its composition is complicated and has many kind of impurities (Song, 2011).

These heavy metals can cause serious environmental problems and influence to ecosystem. Unlike organic pollutants, heavy metals cannot be biodegraded and definitely can cause pollution of air, water and soils. Raj (2013) has investigated sediment contamination of Bera Lake in Malaysia. Bera lake sediment composition reveals that Nickel and Zinc are one of the metallic elements which polluted the Bera Lake. It is also reported that these metallic elements can adverse effect the sensitivity of aquatic species in the lake.

The rapid development in industries mainly in electronic devices to fulfil current technology applications demand are found to increasingly produced heavy metals waste. By considering the environmental pollution, there is a work that focused on the use of these heavy metal in their research. Liu and Ou (2015) have experimentally synthesized nickel zinc ferrite waste from IC lead waste production to transform these waste to valuable magnetic photocatalyst. However, in MREs, there is no literature reported on the possibility of these ferrite waste to be used in MREs. Therefore, in this research, industrial waste nickel zinc ferrite as shown in Figure 2.4 was selected as a new magnetic particle. Recycling of these magnetic particles is beneficial from an environmental point of view as well as economically interesting to reduce cost and additionally guaranteeing sustainability.

Figure 2.4 Waste nickel zinc ferrite particles

2.3 Preparations of MREs

The preparation process to fabricate MREs are shown in Figure 2.5. The process started with weighing raw materials with the exact amount as in formulations. The weighted raw materials were compounded then undergoes cure characteristics measurement. After that, the compounded rubbers were molded and cured to produce final products.

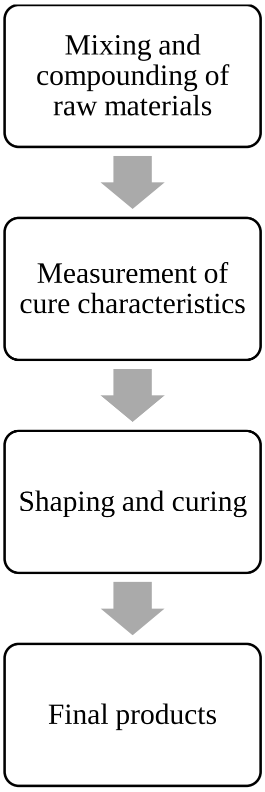


Figure 2.5 MREs production process

2.3.1 Mixing and compounding

Rubber mixing and compounding of MREs is defined as a process of combining elastomers and additives which is accomplished by using conventional rubber-mixing (two roll mill). MREs with good dynamic and mechanical performance requires good dispersion of magnetic filler particles. Mixing is an important step in the production of MREs because of the uniformity, level of dispersion and the consistency of a batch depend on the mixed compound produced (Blow, 1973). During mixing, filler aggregates become uniformly distributed and the polymer is incorporated into the void spaces of the agglomerated pellets, and ultimately the filler agglomerates are broken into distinct aggregates.

Typical rubber mixing and compounding ingredients contains various ingredients to enhance the performance of rubber vulcanizate and improve processability. Table 2.5 shows some of the most used ingredients in rubber mixing and compounding.

Table 2.5 Common ingredients in rubber mixing and compounding (Ciesielski, 1999)

Material	Function	Example
Crosslinking agent	Reacts chemically with rubber to form crosslinks between the rubber molecular chains	▪ Sulphur ▪ Peroxides
Activator	Activate the vulcanization process and speed up the rate of vulcanization	▪ Zinc oxide ▪ Stearic acid
Accelerators	Increase the rate of vulcanization and reduce the sulphur content to achieve optimum vulcanizate properties	▪ Mercaptobenzothiazole (MBT) ▪ Diphenyl guanidine (DPG) ▪ N-cyclohexyl-2-benzothiazole sulfenamide (CBS) ▪ Tetramethylthiuram disulphide (TMTD) ▪ Zinc dibutyl dithiocarbamate (ZDBC)
Antioxidants	Slow down the aging process	▪ *p*-phenylene diamines
Plasticizers	Aid in improving the dispersion of fillers and reduce the viscosity of uncured rubber	▪ Aromatic, naphthenic and paraffinic oil

2.3.2 Measurement of cure characteristics

The degree of vulcanization of MREs compound has a big influence on the properties of final products. The first commercial method for vulcanization has been attributed to Charles Goodyear with his idea to heat natural rubber and sulphur. The vulcanization process was first introduced in Springfield, Massachusetts in 1841. A year later, Thomas Hancock used essentially the same vulcanization process in England (Coran, 1994). Vulcanization is a process to form crosslink between polymer chains resulting increase in elasticity and decrease in plasticity. During vulcanization, the eight-membered ring of sulphur breakdown into smaller part with varying number of sulphur atoms. These parts are quite reactive. At each cure sites on the rubber molecules, one or more sulphur atoms can attach and from there, a sulphur chain can grow until it eventually reaches a cure site on another rubber molecule.

The important characteristics obtained from vulcanization process are the time elapsed before crosslinking occurs, the rate of crosslinks formation, and the extent of crosslinking at the final process. Commonly, these curing characteristics are measured by conventional rubber curemeters such as oscillating disk rheometer (ODR) and moving die rheometer (MDR) (Ciesielski, 1999, Praveen et al., 2009, Karaağaç et al., 2009). Figure 2.6 shows the general curve for vulcanization of rubber which is divided into three stages. The first stage is characterized as induction period which is at this stage, the rubber started to react with other additives and slowly flow to fill the mould cavity then scorch time will be obtained. Second stage involved vulcanization process which the rubber molecular weight started to form crosslinking network structure. The last stage involves over curing reactions which are divided into three types which are marching, stable and reversion. In a stable case, an equilibrium degree of vulcanization is obtained. However, in marching case, additional crosslinks may occur differ with reversion, which the rubber network might break down depending on types of rubber, vulcanization agent and temperature.

In MREs, there is a little work discussed about the curing characteristics of MREs. Borin et al. (2012) investigated the influence of the concentration of the magnetic filler particles on the level of crosslinking of MREs. The measurements have been performed using the mixture of silicon, curing agent and magnetic soft iron powder. It was found that the free movement of magnetic particles in rubber affect the level of crosslinking in MREs. The concentrated MRE samples requires much longer time for hardening and form crosslinking.

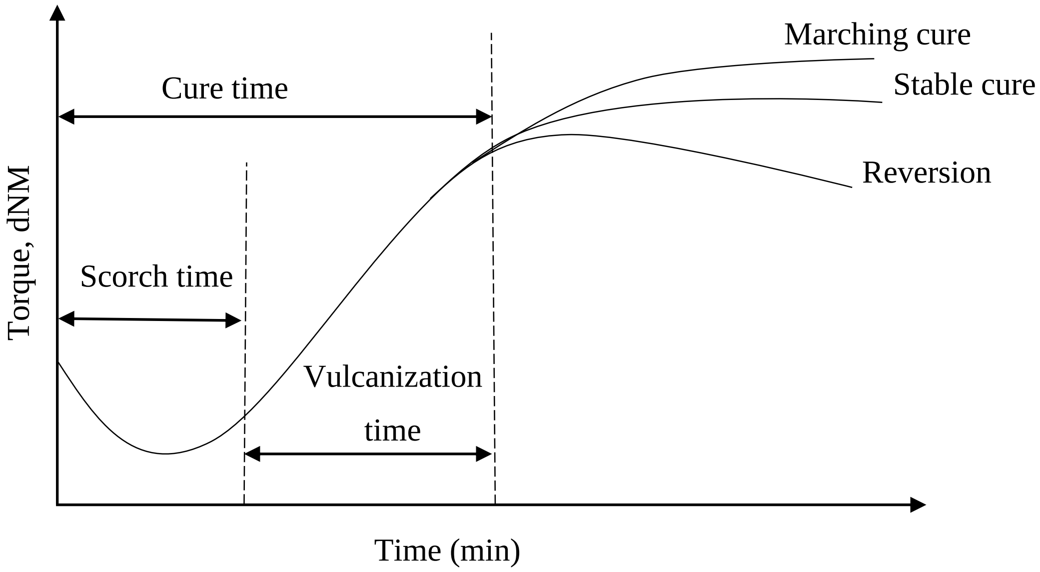


Figure 2.6 Vulcanization curve for rubber (Ciesielski, 1999)

2.3.3 Shaping and curing

After compounding of all formulation ingredients and measurement of curing characteristics, MREs compound undergo shaping and curing process in a compression moulder with a specific plate mould according to desired shape for testing and applications. There are two ways of curing MREs as these materials can be fabricated into two types; isotropic MREs and anisotropic MREs. For isotropic, the compound is cured using conventional way at around 150 ℃ to 170 ℃ under a pressure of approximately 10-12 MPa (Jung et al., 2016, Yunus et al., 2016). A schematic of a compression moulder is illustrated in Figure 2.7. The curing temperature and pressure are crucial to control the compound flow and remove bubbles or any trapped air in the rubber compound. In addition, the defects of rubber vulcanizate that commonly occurred such as bubbles and short mould also can be avoided.