Development and characterization of novel polymeric foams for industrial applications

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DEVELOPMENT AND CHARACTERIZATION OF NOVEL POLYMERIC FOAMS FOR INDUSTRIAL APPLICATIONS

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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Summary

Magnetorheological (MR) materials are known as a group of smart materials that respond to external magnetic field. MR materials consist of magnetically polarisable particles in a non-polarisable matrix. In this work, magnetic foams (MFs), a special type of MR solids, have been synthesized from flexible polyurethanes (PU) foams and carbonyl iron particles. Low and high density MFs have been prepared.

Stereo-zoom optical microscope, scanning electronic microscope (SEM) and X-ray computed tomography (CT) were used to characterize the PU base foams and MFs morphologically. The developed MFs showed acceptable stable structures and relative uniform distribution of the carbonyl iron particles. Thermogravimetric analysis (TGA) was applied to characterize the thermal degradation properties. The apparent activation energy of degradation was calculated by using the Ozawa's method. The carbonyl iron particles were found to improve the thermal stability of magnetic foams in nitrogen. The magnetic foams were observed to have lower activation energy at the earlier degradation stage and higher activation energy at the later degradation stage than pure PU foams in air. The magnetic sensitivity of MFs was tested using the testing jigs that were designed and home-made. The compressive test results showed that strength of the MFs had a slight decrease in the vertical mode but a slight increase in the horizontal one. In summary, the developed MFs were not sensitive enough to respond to the applied magnetic field (approximately 0.2 Tesla).

The sound absorption property, in terms of the sound absorption coefficient (SAC) was examined using an impedance tube. The iron contents were able to influence SAC and the absorbing frequency range of the MFs. The radar absorption property test of the MFs was conducted on a vector network analyzer. The effective but not sufficient radar absorbing ability was observed. The absorbed radar power increased with the iron content proportionally and significantly.

1. Chapter 1 Introduction

1.1 Overview

Smart materials are a group of materials that have one or more properties that can be significantly controlled by external stimuli such as stress, temperature, pH, electric field and magnetic field, et cetera. Magnetorheological (MR) materials are examples of smart materials which are attracting more and more attention due to their controllable rheological properties. MR fluids are the most well known MR materials consisting ferrous particles in a liquid oil matrix. Under an external magnetic field, the attractive inter-particle force aligns the ferrous particles into chains and the shear modulus of the MR fluid is then increased. After removal of the external magnetic field, the fluid returns to the original liquid state. Similar to MR fluids, MR elastomers (MREs) have been reported in the literature recently [1, 2, 3] to have effective modulus increase under external magnetic field.

Magnetic foams (MFs) are another new type of MR materials, which use polymeric foams as the non-polarisable matrix instead of elastomers as for MREs. However, the synthesis and properties of such magnetic foams haven't been reported up till now. For this reason, the development of MFs was initiated by our NTU group in July 2004. MFs of low nominal density (20 kg/m^3) with a maximum iron content of 25 wt% (with respect to Polyol involved) were synthesized and a few dampers were designed using the MFs to examine the properties of MFs. However there are still many unsolved technical issues, such as the difficulty in loading higher contents of iron particles, non-uniform distribution of the iron particles, insufficient magnetic field strength produced by the dampers, et cetera. In August 2006, an agreement to develop MFs and their potential applications was signed by Singapore Technologies Kinetic (STK) and Nanyang Technological University (NTU).

MFs of higher nominal density (30 and 55 kg/m^3) with three different iron contents (25 wt%, 50 wt% and 75 wt%) have been successfully synthesized by the author. The physical, morphological, thermal, sound and radar absorption properties of these MFs have been examined and observed. The mechanical properties of the

MFs under an external magnetic field were also tested using the in-house built jigs on an Instron testing machine.

1.2 Objectives

The objectives of this work are:

- (1) to synthesize novel MFs with different iron particle loadings;
- (2) to characterize and study the properties of MF; and to explore the possible applications of MFs

1.3 Scope

The scope of this work covers the following:

- (1) to synthesize magnetic foams from flexible polyurethanes foams and carbonyl iron particles;
- (2) to test the physical, morphological, thermal, mechanical (under a magnetic field) and absorptive (sound and radar) properties of the developed MFs; and
- (3) to analyze and summarize the properties and mechanisms behind the influences of the iron contents on the tested properties

1.4 Report outline

Chapter 1 gives an overview of the project objectives, scope and a description of the report layout.

Chapter 2 provides the literature review on the polyurethane foams and MR materials.

Chapter 3 details the starting materials, experimental procedures and testing techniques.

Chapter 4 discusses the experimental results and observations.

Chapter 1 Introduction

Chapter 5 summarizes the findings of the project and chapter 6 proposes some future works.

2. Chapter 2 Literature Review

This chapter provides a fundamental background of flexible polyurethane foams and MR materials. The basic chemistry, essential components of the synthesis formulation, foaming process and applications of flexible PU foams are reviewed in section 2.1. MR materials and magnetic foams are briefly introduced and compared for their advantages and disadvantages in section 2.2.

2.1 Flexible Polyurethane foams

2.1.1 Introduction to flexible Polyurethane (PU) foams

Flexible PU foams are three-dimensional agglomerations of gas bubbles, separated from each other by thin sections of polymer. The main reactants for the synthesis of flexible PU foams are liquid polyisocyanate and liquid polyol resin in the presence of a number of other necessary additives such as blowing agent, catalyst and surfactant. Thus they are considered as synthetic materials that are both chemical and physical complexes. As demonstrated in Figure 2.1, a typical flexible PU foam structure contains the void areas that are defined as “windows” and the thin polymer structures that are defined as “struts”. The structural unit is a “cell” while the polymer struts are also called “cell walls”.

Figure 2.1 SEM micrograph of typical pure flexible PU foam at 100X magnification

Chapter 2 Literature Review

The fundamental polymerization reaction of alcohols and diisocyanates to produce high-polymers was discovered by Otto Bayer and his co-workers in 1937 [4]. By 1941 the group had succeeded in producing the first laboratory flexible PU foam [5]. By 1954 commercial quantities of flexible PU slabstock foams were produced based on aromatic polyisocyanate with polyester-type polyol to supply the rapidly growing industrial applications.

The first batch of PU foams developed in 1950s was not strong and could not be used at many in-use temperatures and under humidity condition [6, 7]. With the improvement and advancement of new technology and techniques, in particular the introduction of polyether-based polyols, high-purity isocyanates, new catalysts and silicone-based surfactants, it is now possible to produce commercial quality of flexible PU foams economically [8].

2.1.2 Basic chemistry of flexible PU foams

The main reaction for PU chemistry is the reaction between isocyanates and active hydrogen-containing compounds (usually polyol). The highly reactive isocyanate groups ($-\text{N}=\text{C}=\text{O}$) react readily with the hydrogen atoms of polyol [8].

2.1.2.1 The Polymerization reaction

The urethane forming reaction between an isocyanate and an alcohol is shown as follows:

The following reaction illustrates the polymerization of PPG and 2, 4-TDI.

Polyurethane

As shown in Figure 2.2, the polyol portions of the polymer network refer to as the “soft-segments” and the isocyanate portions refer to as the “hard segments”. The covalent bonds hold the PU molecules together, while hydrogen bonding also contributes greatly to the final properties and performance of the PU foams [8].

Figure 2.2 Crosslinking structure of the PU polymers

2.1.2.2 The Gas-producing reaction

To achieve a porous three dimensional foam structure, the PU polymer must be expanded or “blown” by the bubbles and gas produced in the foaming reaction. Carbon dioxide can be generated from the reaction of an isocyanate group with water, shown in Equation 2.3 below:

The intermediate product of this reaction, carbamic acid is thermally unstable. Thus, it spontaneously decomposes to an amine and carbon dioxide and generates heat. Carbon dioxide diffuses into bubbles that were nucleated in the reacting medium, resulting in the expansion or rising of the foam. The produced heat in Equation 2.3 is useful in kinetically driving the reactions and promoting the additional expansion of the gas filled bubbles.

2.1.3 Essential components of flexible PU foam formulation

Flexible PU foams are synthesized from a formulation or a recipe that contains the amounts of the essential ingredients. The essential chemicals involved in the formulation are polyol (PPG), isocyanate (TDI), silicone surfactants (L580 and L600), water, and catalysts including amine catalysts (A210, or A1 and A33) and tin catalyst (D19). The general role and utility of each class of foam making components are discussed below.

2.1.3.1 Polyol (PPG)

Polyol is the first main component in manufacturing the flexible PU foam. Polyol is a source of hydroxyl or other isocyanates reactive groups. Processing and properties of the resultant foam can be significantly affected by the different starting polyol. 90% of the flexible PU foams in the market are made from polyether-type polyols, while the other 10% are polyester-type polyols.

A polyether polyol is the polymeric reaction product of an organic oxide and an initiator compound containing two or more active hydrogen atoms [8]. Commercially, propylene and ethylene are the most widely used oxides to produce polyol. Polypropylene glycol (PPG) was the polyol used in this study.

Polyol is classified by the molecular weight. With the increasing amount of propylene oxide or ethylene oxide during the polyol manufacturing process, the molecular weight increases, resulting in a decreasing reactivity, hardness and an increasing tensile elongation. The molecular weight of the PPG used in this study is 3000, which is the most widely used molecular weight for flexible PU foams of all density range.

The primary function of the polyol is to control the physical properties of the flexible PU foam. It reacts with isocyanate to form urethane links for the soft segments of the PU foam.

2.1.3.2 Isocyanate (TDI)

The second main component for foaming reaction is the isocyanate. Isocyanate provides NCO groups to react with the functional groups from the polyol and other ingredients in the formulation. All the available isocyanates used in today's industry have at least two isocyanate groups per molecule [8]. The two types of the isocyanates for flexible PU foam in the market are toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI). TDI is the most commonly used isocyanate and MDI is for high-resiliency, semi-flexible and microcellular foams [8]. The isocyanate used in this project is TDI.

The two most important isomers of TDI are 2, 4-TDI and 2, 6-TDI. The pure 2, 4 isomer is more reactive than the pure 2, 6 isomer. The main ingredient for manufacturing TDI is toluene. Figure 2.3 depicts the chemical structure of the two isomers of TDI.

Figure 2.3 Isomers of TDI

The primary function of TDI is to control the firmness of the PU foam. It reacts with polyol to form urethane links for the soft segments of the PU foam.

TDI is a harmful, corrosive chemical which may cause severe burns to mouth, esophagus and stomach discomfort if swallowed, moderate to severe eye irritant, moderate to severe skin irritant and sensitizing after inhalation.

2.1.3.3 Silicone surfactants (Niax[®] L580 and L600)

Flexible PU foams are made with the aid of non-ionic silicone-based surfactants, which are non-hydrolysable and water-amine premix stable [8]. The functions of silicone surfactants in broad terms are listed as below [8]:

- i. Lower surface tension,
- ii. Emulsify incompatible formulation ingredients,
- iii. Promote nucleation of bubbles during mixing,
- iv. Stabilize the rising foam by reducing stress in thinning cell walls,
- v. Counteract the defoaming effect of any solids added to or formed during the foam reaction.

Stabilization of the cell walls is the most crucial function of the silicone surfactants. Coalescence of the growing cells during the foaming reaction would take place if the cells are not sufficient strong through the polymerization process. A minimum amount of surfactants are necessary to produce structural successful foams. However, excessive surfactant levels would lead to over-stabilized status of the cells, resulting in tighter foams with diminished physical properties. Thus, an optimum surfactant concentration is very crucial for producing stable and open-celled flexible PU foams [8].

There are seven types of silicone surfactants for consideration, each having different efficiency and capacity for making porosity of foams (Figure 2.4). L580 was the silicone surfactant for low density foams with the density less than 20 kg/m³ in previous work, and L600 was for higher density foams with the density larger than 30 kg/m³ in current development of MFs.

Figure 2.4 Influence of various silicone surfactants on the efficiency and porosity of flexible PU foams [9]

2.1.3.4 Water (deionized water)

Water offers active hydrogen in the reaction with isocyanate, and produce carbon dioxide gas in Equation 2.3. The gas diffuses into the nucleated bubbles and aids in foam expansion.

2.1.3.5 Catalysts

All commercial flexible PU foams are produced with the aid of catalysts. Amine and tin catalysts are the most useful and essential two classes for flexible PU foams.

The major purpose of using catalysts is to balance the rate of the chain propagation reaction and rate of the blowing reaction. The chain propagation reaction refers to the reaction between isocyanate and polyol, while the blowing reaction associates to the reaction of isocyanate with water [8]. Catalysts act as the controller to monitor the balance of the two rates so that the gas entrapped in the gelling polymer is efficient to produce desired porous structure, while the foam cells also have sufficient strength to become self-supporting without

collapse or shrinkage. Another role of surfactants is to ensure that the curing (reaction) process is completed in the finished foam [8].

i. Amine catalysts (Niax[®] A210, or A1 and A33)

Tertiary amines are the most commonly used catalysts for flexible PU foams, and usually offer contribution to the gelling reaction as well. The catalytic activity of amines is due to the free electron pair on the nitrogen atom in their chemical structure (Figure 2.5).

Figure 2.5 Free electron pair of tertiary amines

The type and concentration of amines depend on the requirement process such as rise profiles, gel times, and so on. Choice of the amine catalysts may affect the mechanical properties of the finished foam (e.g. airflow and load bearing) through their influence on the primary and secondary foam reactions [10]. A210 was used for the low density foams with the density less than 20 kg/m³ in the previous work [11], while A-1 and A-33 were for higher density foams with the density larger than 30 kg/m³ in the current development of MFs.

ii. Tin catalysts (Niax[®] D19)

Organometallic catalysts are the main components that promote the gellation reaction between isocyanate and polyol during the foaming process. Tin salts are the preferred gelling organometallic catalysts, particularly tin compounds. The most common types are stannous octoate (Niax[®] D19) and Dibutyltin dilaurate (Niax[®] D22), which are designed for conventional flexible foam applications. D19 was the tin catalyst used in this project.

The primary function of D19 is to promote the gellation reaction. Insufficient gellation to balance the gas evolution reaction would result in foam splits. Small increase in D19 will give good open-celled foams. But further increase will speed up the gellation reaction and tighten the foam and result in severe shrinkage.

2.1.4 Foaming process of PU foams

Figure 2.6 illustrates the formation process with various events leading to the synthesis of flexible polyurethane foams. Cells in the final foam are produced by blowing agents. Bubbles that are produced by gas diffusion are nucleated into the system at the time of mixing. The bubbles grow to a final size controlled by the amount of blowing agent available, the exothermal and the degree of bubble stabilization. Polymer morphology developments and mechanical factors govern the degree of cell-openness in the final foam. The detailed explanation and steps of foaming process are given in Section 3.3 of this thesis.

Figure 2.6 Foaming process of flexible polyurethane foams [8]

2.1.5 Applications of PU foams

Based on the combination of density and stiffness, Polyurethane products have many uses in different aspects. Over three quarters of the global consumption of polyurethane products is in the form of both flexible and rigid types foams. In both cases, the PU foams are usually combined with other materials in the applications. For example, flexible foams are behind upholstery fabrics in commercial furniture while rigid foams are inside the metal and plastic walls of refrigerators and freezers, or behind paper, metals and other surface materials in the case of thermal insulation panels. Polyurethane is also used for moldings which include door frames, columns, balusters, window headers and so on. Table 2.1 illustrates the application classification of PU materials in terms of their density and stiffness.

Table 2.1 Chart of applications of PU materials

Density of PU foams	Flexible	Semi-rigid	Rigid
Low density Foams (6 kg/m ³)	High resiliency foam for bedding and upholstery	Packaging foam	Insulation foam
High density Foams (400 kg/m ³)	Footwear midsoles/outsoles	Integral skin foam for vehicle interiors	Simulated wood
Microcellular foams and Elastomers (800 kg/m ³)	Fabric coatings and synthetic fibers vehicle facia and other exterior parts		Structural foam
Solid PU Elastomers (1200 kg/m ³)	Print roller	Cast elastomers: coatings, adhesives and sealants	RIM solid plastics

Current PU foams possess numerous qualities such as resistant to moisture and odour-formation, durable, easily shaped and fabricated, which made it a suitable candidate for cushioning materials for furniture, transportation and packaging applications [8]. Table 2.2 manifests a list of example applications of flexible PU foams.

Table 2.2 Example Applications of flexible PU Foams

Application Types	Examples
Furnishing	carpet, bedding, furniture, padding
Transportation	crash pads, filters, steering wheels
Others	diapers, ear plugs, toys

2.2 MR materials and magnetic foams

Magnetorheological (MR) technology was pioneered by Jacob Rabinow in the 1948 [12]. However, the technology was not fully used until in the late 1980s and

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1990s when researchers began to develop the commercial viability of MR fluids (MRF) [13]. Today, a lot of MR materials can be found, and the most commonly used one is MR fluid. MR fluid has already been commercialized and it is used in many applications such as damping, densimetric separation, heat transfer, levitation, and quality control (Turbine Blade Inspection), etc [14].

Further research on this phenomenon have produced some other products namely MR elastomer (MRE), MR sponge and magnetic foam (MF). The principles of these products are similar. By using a magnetic field to align the iron particles inside the products, the product will become harder and stiffer. When the magnetic field is released, the product will transform back to its original state.

The main difference between these products is the medium of the iron particle. In MR fluid, the iron particles are suspended in a liquid medium such as oil, synthetic oil, water, or glycol. MR sponge is a further development of MR fluid. In MR sponge, MR fluid is injected into an absorbent matrix (a sponge), keeping the MR Fluid inside. In MR elastomer the medium is natural or synthesized rubber, while for magnetic foam the main medium is flexible PU foam.

Nowadays researchers have been successful in applying the MR technologies. For example, MR Fluid dampers are currently used in buildings to mitigate resonance caused by high wind and seismic activities. Sponge-based MR dampers have also been applied to reduce vibrations in home appliances i.e. washing machines. Some research had also been done in applying MR Fluid damper into car suspension system.

2.2.1 MR fluids (MRF)

The initial discovery and development of MR fluids and MR devices were pioneered by Jacob Rabinow at the US National Bureau of Standards in 1948 [15]. However, after the initial discovery by Rabinow, not much information had been published on MRF. Only until late 1980s and 1990s researchers started to get serious in developing the application of MR technology [13].

A MRF is a suspension in a non-magnetic low viscosity liquid medium (e.g. mineral oil, synthetic oil water or glycol), which typically contains micron-sized magnetizable particles (commonly carbonyl iron) [12]. The MR effect was schematically illustrated in Figure 2.7. In the absence of a magnetic field, MRF behaves similar like motor oil, presenting Newtonian fluid characteristic. When a magnetic field is applied, the iron particles inside the suspension will align themselves under the attractive inter-particle force according to the magnetic field direction.

Figure 2.7 MR effect. (a) MRF without magnetic field; (b) MRF with magnetic field

The maximum yield strength produced by MRFs could vary in the range of 50-100 MPa for applied magnetic field values of 150-250 kA/m [13]. The ultimate strength of MRFs is limited by the magnetic saturation of the particles suspended in the fluid. When it is sheared under a stress above its yield stress, it will show characteristics of the liquid phase again and the yield stress is determined by the external magnetic field [16]. MRFs can be operated in the temperature ranging from -40°C to $+150^{\circ}\text{C}$ with only slight variation in the yield stress [16].

One of the advantages of MRFs is that they are not sensitive to contaminants or impurities during the manufacture process and usage. In addition, since the magnetic polarization mechanism is not affected by the surface chemistry of surfactants and additives, stabilization of MRFs against particle-liquid separation is not a problem in spite of the density mismatch between the magnetizable particles and carrier liquid [16].

A major limitation of MRFs is the sedimentation of the magnetizable particles due to gravitational settling. This happens due to a density mismatch between the

solid particles and the carrier liquid. To reduce the phenomenon, a magnetorheological grease (MRG) – based MR damper was developed by Zhu [16]. The MRG was shown to greatly reduce the sedimentation effect of the MRF on the rotor dynamic behaviors [17]. Beside that, other compliment additives are also needed to promote particle suspension, enhance lubricity, modify viscosity and inhibit wear [18].

2.2.2 MR elastomers (MREs)

The development of MREs was inspired by the success of the MRFs. Instead of using fluid as its carrier, MREs use solid, polymer or gel-like based material to carry the magnetizable particles. At the Ford Research Laboratory, Ginder, et al. have developed MRE composite composed of natural or synthetic rubber filled with micron-sized iron particles in 1999 [2]. The particles were aligned in chains by the imposition of a magnetic field during the curing of the MREs. The produced MRE composites were reported to possess field-dependent mechanical moduli, anisotropic mechanical and magnetic properties.

Under an applied magnetic field, the particles inside MREs are magnetized, resulting in magnetic dipole moments pointing along the magnetic field. However, after the full curing of the MREs, the particles become locked by the crosslinked solid polymer matrix in their position. For this reason, the particles have to be aligned by a magnetic field before the curing of the MREs in the earlier reports [19]. However, M. Lokander, B. Stenberg found that MRE materials with large irregular particles had significant MR effect without pre alignment of the particles [19], and the MR effect could be increased by the addition of plasticizers [20].

The mode of operation for MRE and MRF is one of the distinct differences between these two types of MR materials. The particle chains within the MREs are operating in the pre-yield state while MRFs typically work within a post-yield continuous shear or flow regime [19]. The characterized strength of MRF is the magnetic field-dependent yield stress while MREs are characterized by the field-dependent shear stress modulus [16].

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Unlike MRFs, the particles inside MREs do not produce sedimentation due to the solid characteristic. In addition, sealing is not a crucial consideration for MRE applications. Thus the MREs are interesting candidates for the active stiffness and vibration control of structural systems.

2.2.3 MR sponges

MRF is constrained by capillary force in an absorbent matrix (e.g. a sponge, open-celled foam, felt or fabric) in the MRF sponge devices [16]. The sponge serves to keep the MRF located in the active region of the device where the magnetic field is applied. Application of the external magnetic field enables the MRF in the matrix to develop both yield strength and resist shear motion [16]. The sponge allows MRF to be operated in a direct shear mode without seals, bearings or precision mechanical tolerances [21]. Besides that, MR Sponge also can greatly eliminate the sedimentation problem which often occurs in MRFs.

MR sponges are more advantageous than MRFs as they cut the cost used for the sealing elements associated with fluid filled devices. MR sponges are generally used for applications where less force and higher degree of control is required. The other advantage is that MR sponges will cause little wear after long period usage in a shear mode. This is because the sponge materials also absorb the stress received besides the iron suspension itself. MR sponges require only small amount of MRF, which saves the cost in producing the MR sponges. However, as the less amount of MRF is used, the strength of MR sponges would also be relatively smaller.

One main disadvantage of MR sponges is that due to the open structure of the absorbent matrix, leaking is still possible when they are compressed. Again, this would bring back to the sealing problem like in the MRFs.

2.2.4 Magnetic foams (MFs)

MFs are made of flexible PU foams with magnetizable carbonyl iron particles embedded inside the polymeric cell walls. The main difference between MFs and

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MFs is the solid and liquid characteristics of the two classes of materials. This makes MFs more versatile and also easier to maintain. There is no problem of particle sedimentation in MFs. Besides that, a MF device could be easily made at a relatively cheaper cost than that of MR Fluid or MR Sponge, without the leaking-preventing elements.

Being the same as MREs, the iron particles are fixed within the polymeric matrix in MFs. However, MFs combine the properties of the flexible foams, such as soft, light weighted, porous, energy consumable, easy cutting, etc. it enables MFs to be candidates in different application aspects where they require softness, light-in-weight, porosity, and so on.

One drawback of MFs is that it is difficult to distribute the iron particles evenly inside the polymer cell walls, due to the porous structure of the MFs. This might cause unequal property in different part of the foam. Another limitation of MFs is that the amount of iron particles that can be added is also limited. Excessive iron particles inside the foams would lead to structural failure. Lastly, the fatigue life of MFs is also limited. The stiffness and strength of MFs are supposed to decrease after multiple usages.

The characteristics of the four types MR materials were summarized in Table 2.3. Like MREs, MFs have the advantage of non-sedimentation and non-leaking due to the solid medium to carry the iron particles. Together with the flexible foam properties, different applications of MFs could be explored and implemented commercially. However, due to the porous foam structure, iron particles could only be wrapped in the thin cell walls and thus the air windows limit the iron volume fraction in the whole. The embedded iron particles might affect the thermal and mechanical properties of MFs as well. Optimization of iron particle loading, control of cell sizes and cell walls are necessary for the applicable MFs.

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Table 2.3 Summary of the characteristics for the four types MR materials

MR materials	Descriptions	Advantages	Disadvantages
MRF	<ul style="list-style-type: none">• suspension containing magnetizable particles in non-magnetic liquid medium	<ul style="list-style-type: none">• responds to magnetic field instantaneously• insensitive to contamination	<ul style="list-style-type: none">• susceptible to sedimentation• expensive
MRE	<ul style="list-style-type: none">• composed of natural/synthesized rubbers with iron particles embedded in it• iron particles are aligned before the rubber curing• possess field-responsive anisotropic and magnetic properties	<ul style="list-style-type: none">• equally distribution or columnar chain-like arrangement of the particles• no sedimentation of particles• no means of sealing is required during MRE application	<ul style="list-style-type: none">• After the elastomer is cured, the particles become locked in their place• limited increment of the shear stress modulus
MR Sponge	<ul style="list-style-type: none">• constrain MR Fluid by capillary action in an absorbent spongy matrix• MRF is kept by sponge in the active region during operation	<ul style="list-style-type: none">• Allowing MRF to be operated in a direct shear mode without seals, bearings or precision mechanical tolerances• Elimination of the particle sedimentation• Little wear after long period usage in shear mode	<ul style="list-style-type: none">• leaking of MRF when MR sponge is compressed• applications where less force higher degree of control is used
MF	<ul style="list-style-type: none">• composed of flexible polyurethane (PU) foam and micron-sized carbonyl iron particles• synthesized and developed for different iron particle loadings	<ul style="list-style-type: none">• No sedimentation or leaking problems due to the solid foam matrix• Combined properties of flexible foam like soft, light weighted, energy consumable, easy cutting, etc	<ul style="list-style-type: none">• difficult to distribute the iron particles evenly inside the foam• Limited loading of iron particles• Limited fatigue life of the foam

2.3 Possible Applications of MFs

A possible application of MFs would be hardness-adjustable cushions. This is provided if MFs can show the same MR effect as discussed in section 2.2.1, that by exerting an external magnetic field, the iron particles in the MFs might be able to align themselves, thus increasing the modulus of the MFs.

The below sections describe other possible applications of MFs.

2.3.1 Sound absorption

Sound-absorbing materials, also known as sound absorbers, are defined as materials with high sound absorption coefficients (SAC) [22]. Currently there are mainly three groups of existing sound absorbers: porous absorbers, panel absorbers and resonators [23]. The characteristics and comparison of the three groups are tabulated in Table 2.4. Flexible open-cell PU foams with their 3D network structure are a typical group of porous absorbers. With the main advantages of excellent absorption over wide range of medium and high frequency, flexibility and low cost, flexible open-cell PU foams have very wide applications in sound absorption and noise control.

Table 2.4 Characteristics of the three groups of sound absorbers

Sound Absorbers	Examples and Descriptions	Advantages	Disadvantages
Porous absorbers	<ul style="list-style-type: none">• Most commonly used sound absorbers;• Carpet, spray-applied cellulose, glass fiber, open-cell foam, and felted or cast porous ceiling tile	<ul style="list-style-type: none">• Excellent performance for medium and high frequency sound absorption (>500 Hz);• Low cost• Flexible shaping control and light weighted;	<ul style="list-style-type: none">• Poor performance at low frequencies, especially at very low frequency range (< 250 Hz)• bulky structure
Panel absorbers	<ul style="list-style-type: none">• Typically non-rigid, non-porous materials which are placed over an airspace that vibrates in a flexural mode in response to sound pressure exerted by adjacent air molecules• thin wood panelling over framing, lightweight impervious ceilings and floors, glazing and other large surfaces capable of resonating in response to sound	<ul style="list-style-type: none">• Excellent absorption for very low frequency sound (< 250 Hz)• Thin layer structure• Large surface coverage	<ul style="list-style-type: none">• Poor absorption for mid frequency sound (500 Hz – 1000 Hz)
Resonators	<ul style="list-style-type: none">• Typically act to absorb sound in a narrow frequency range (e.g. Helmholtz resonators)• some perforated materials and materials that have openings (holes and slots)	<ul style="list-style-type: none">• Able to applied to specific low frequency range, and can be broadened over the frequency by lining the cavity with sound absorbing materials	<ul style="list-style-type: none">• Narrow applicable frequency range;

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There are two available sound absorption mechanisms for porous absorbers [23, 24, 25]. The first one is the viscous dissipation in the air cavities. The air flow is disturbed during the sound propagation. The second one is friction due to the vibrating pore frames, resulting in temperature rise. Both of these two mechanisms convert the sound energy into heat energy, through the air flow viscosity and thermal conduction.

The core application of sound absorbers is noise control. By different sound frequency range, noise can be classified into three types, detailed in Table 2.5.

Table 2.5 Applications of sound absorbers, classified by sound frequency range [26]

Noise type	Frequency range	Examples
Typical low to medium frequency noise or rumble	0 to 500 Hz	compressors, grinders, crushers, engines, presses and exhaust fans
Mid-range hum or chatter	250 to 2,000 Hz	office machinery, circular saws, human voice
High frequency squeal	1,000 to 4,000 Hz and above	ultrasonic welders, hydraulic pumps, fast small engines, some industrial cutting and polishing processes

Flexible PU foams are good sound absorbers of medium and high frequency sounds. By surrounding, panelling or cladding, flexible PU foams are able to lower the noise levels of machinery, instruments, sound studios and earthmoving equipment cabins, vehicle interiors and so on.

SAC is defined as is the ratio of the sound energy absorbed by a surface of a medium or material to the sound energy incident on the surface [23]. The mathematic expression of SAC α is:

$$\begin{aligned} \alpha &= \text{absorbed sound energy} / \text{incident sound energy}; \\ &= 1 - r^2, \text{ where } r \text{ is the reflection coefficient.} \end{aligned} \tag{Equation 2.4}$$

There are two common testing methods to measure the SAC [27]: reverberation room method for random incidence SAC and impedance tube method for normal incidence SAC.

Impedance tube measurement is selected in this work, because this device is easy to operate and inexpensive. Moreover the impedance tube technique has the advantage of comparative measurements between different materials, and the effects of varying the certain parameters, e.g. sample thickness, air gaps etc. However the main disadvantage of this measurement is that only normal incidence SAC is measured, i.e. it is the restricted evaluation which is not representative for practical cases.

2.3.2 Radar absorption

Electromagnetic interference (EMI) is a serious problem in the applications of electromagnetic wave in the gigahertz range, especially for communication equipments [28]. Electronic devices have been developed with electromagnetic compatibility (EMC) to overcome EMI. Electro-magnetic compatible devices can be defined as those that emit no harmful electromagnetic waves outside but at the same time protecting its cores from the harmful electromagnetic waves generated from the other devices. EMC can be achieved by the use of electromagnetic wave absorbers. Absorbers minimize the electromagnetic reflection from the metal plate such as aircrafts, ships, tanks and the walls of anechoic chambers and electronic equipment.

Microwaves are electromagnetic waves within the frequency range from 0.3 GHz to 300 GHz (Figure 2.8). This includes ultra-high frequency (UHF) (0.3–3 GHz), super high frequency (SHF) (3–30 GHz), and extremely high frequency (EHF) (30–300 GHz) signals.

Figure 2.8 Electromagnetic wave spectrum

The term RADAR was coined in 1941 as an acronym for “radio detection and ranging”. Radar is an object detection system that employs electromagnetic waves to identify the range, altitude, direction, and or speed of moving and stationary objects such as aircraft, ships, motor vehicles, weather formations, and terrain.

A radar system has a transmitter that emits microwaves or radio waves. These waves are in phase when emitted, and when they come into contact with an object the waves are scattered in all directions, some of the waves are reflected back and it has a slight change of wavelength (and frequency) if the target is moving. Radar is used in meteorological precipitation detection, measuring ocean surface waves, air traffic control, traffic police speed detectors and the military.

2.3.2.1 Radar absorbing materials

Radar absorbing materials or electromagnetic wave absorbers, containing resistive and sometimes magnetic substances, are used on military vehicles to reduce radar reflection. The existing radar absorbing materials can be classified into three groups: iron ball paint, foam absorbers and Jaumann absorber (Table 2.6) [29, 30].

Table 2.6 Classification and characteristics of radar absorbing materials

Radar absorbing materials	Examples and Descriptions	Characteristics and Applications
Iron ball paint	<ul style="list-style-type: none">• tiny spheres coated with carbonyl iron or ferrite• molecular oscillations from the alternating magnetic field, which leads to conversion of the radar energy into heat	<ul style="list-style-type: none">• Thin layer painting without degrading the aerodynamic performance• Suitable for coating of military aircrafts
Foam absorbers	<ul style="list-style-type: none">• used as lining of anechoic chambers for electromagnetic radiation measurements• typically consists of a fireproofed urethane foam loaded with carbon black, and cut into long pyramids• attenuates signal by two effects: scattering and absorption	<ul style="list-style-type: none">• Able to work at broad band radar frequency• Able to be easily manufactured into desirable shapes• Applied in anechoic chambers and not suitable for coating due to the bulky thickness
Jaumann	<ul style="list-style-type: none">• a resonant radar absorbent device	<ul style="list-style-type: none">• Single-layered design only works

absorbers (or Jaumann layer)	<p>(e.g. Salisbury screen)</p> <ul style="list-style-type: none">• consisted of two equally-spaced reflective surfaces and a conductive ground plane• uses wave interfering to cancel the reflected wave	<p>at single radar frequency;</p> <ul style="list-style-type: none">• Multi-layered Salisbury designs can cover a band of frequencies, but only by increasing the thickness, and the best cover only a fraction of the radar spectrum;
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2.3.2.2 Carbonyl Iron Particles

Carbonyl iron particles are the main radar absorbent component of the iron ball paint. One of the important applications of carbonyl iron particles is microwave absorption, especially in the frequency range of 2.6–18 GHz, which falls in the range of the electromagnetic waves in the radar systems [31]. Thus it has been widely applied in the field of electromagnetic shielding and absorbing materials. Special attention had been given to electromagnetic wave absorbers consisting of composites, because of the simplicity for making a complex shape and a tailored design and also the control of absorption properties by changing the content of magnetic materials [32-36].

Permittivity (dielectric constant) and permeability are the most important electromagnetic properties for radar absorbing materials. Many researchers have reported that the experimental permittivity and permeability of their radar absorbing materials were dependant on the frequency range. Feng et al. have synthesized carbonyl iron/rubber radar absorbing materials and tested the effective complex magnetic permeability and dielectric permittivity spectra with various carbonyl iron volume fractions by using the transmission/reflection method with a vector network analyzer [37]. It was found out that an increase in carbonyl iron content reduces the minimum reflection loss from 1.3 to 23.9 dB and shifts the frequency of the minimum reflection loss from 15.5 to 3.5 GHz. S. Kimura et al have also synthesized carbonyl iron-ferrite/PMMA composites fabricated by a hybridization method and reported that the reflection loss less than 20 dB could be achieved in a frequency range of 1.7–5.0GHz when the composite thickness was below 5.00 mm [38].

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Magnetic foams are a group of such composites. By combining the characteristics of carbonyl iron particles and flexible PU foams, MFs have great potential to be developed into a functional radar absorber.

2.3.2.3 Magnetic Foams (MFs)

As mentioned in previous sections, MFs are composed by flexible PU foam as the polymer matrix and carbonyl iron particles as the magnetic fillers. The MFs to be studied are low density MFs with SA carbonyl iron, and high density MFs with BASF ER carbonyl iron, which are especially suitable for microwave absorption application. Radar absorption tests will be conducted for the low and high density MFs using the method of generalized scattering matrix and mode-matching from a 2-port device.

3. Chapter 3 Experimental

This chapter describes the materials used to synthesize magnetic foams and the procedures of the experiments. Section 3.1 gives the starting materials while 3.2 provides the procedure flow. Sections 3.3 and 3.4 describe the synthesis process and characterization in detail.

3.1 Materials

The main reactive components to synthesize PU foams were the commercially available Polyol (PPG, Caradol SC56 - 01, Seraya under Shell) and isocyanate (TDI, toluene 2, 4 diisocyanate, Sigma Aldrich). Two types of additive iron particles were applied: carbonyl iron from Sigma Aldrich with an average diameter of 4.5 μm ~ 5.2 μm ; carbonyl iron grade ER from BASF with an average diameter of 4 μm (narrow particle size distribution). Other essential chemical components such as silicon surfactants (Niax[®] L580 and Niax[®] L600), tin catalyst (stannous octotrate) (Niax[®] D-19) and amine catalysts (Niax[®] A210, A-1, A33) were provided by Momentive Performance Materials.

3.2 The procedure flow

The essential chemical components to synthesize MFs were first weighed and then mixed in the fume hood. After the natural curing and post curing process, the MFs with different iron contents were formed and they were ready to be cut into required dimensions. Their physical, morphological, thermal and mechanical properties were examined. The techniques and equipments used for each type of MF properties are listed in Table 3.1.

Table 3.1 Techniques and Equipments for MF properties

Property Classification	Properties	Techniques and Equipments
Physical properties	Colour Density	Ruler; Weighing balance
Morphological properties	Macro surface morphology Micro surface morphology 3D morphology	Stereo-zoom optical microscope; Scanning electronic microscope (SEM); X-ray Computed Tomography (CT)
Thermal properties	Thermal stability	Thermogravimetric Analysis (TGA)
Mechanical properties With a magnetic field	Magnetic sensitivity	Home-made testing jigs; Instron testing machine
Acoustic properties	Sound absorption	Impedance tube
Electromagnetic properties	Microwave absorption	Agilent network analyzer

3.3 Synthesis procedures of MFs

3.3.1 Sample naming

The naming of the MF samples used in this report is given in Table 1. The number 30 in the name of MFXX-30 refers to the nominal density of 30 kg/m³ for the low density MFs, which is the desired density of a PU foam before adding iron particles. Similarly the number 55 in MFXX-55 refers to nominal density of 55 kg/m³ for the high density MFs. XX in the name refers to the content (in wt%) of iron particles based on the amount of polyol. For example, when 100 g of polyol is required in a formulation for a 30 kg/m³ PU foam and 50 g of iron particles is added, the sample name is denoted as MF50-30.

Table 3.2 Sample names and composition of PU foams and MFs

Sample names		Composition
PU-30		Pure PU with 30 Kg/m ³ (nominal density)
MFXX-30s	MF25-30	PU-30 + 25 wt% iron particles
	MF50-30	PU-30 + 50 wt% iron particles
	MF75-30	PU-30 + 75 wt% iron particles

PU-55		Pure PU with 55 Kg/m ³ (nominal density)
MFXX-55s	MF25-55	PU-55 + 25 wt% iron particles
	MF50-55	PU-55 + 50 wt% iron particles
	MF75-55	PU-55 + 75 wt% iron particles

3.3.2 Low density MFs (MFXX-30s)

The synthesis procedures for low density MFs were designed based on a typical foaming process for PU foams. Iron particles were added into the mixture of polyol, de-ionized water, amine catalysts and surfactants. TDI and tin catalyst were weighed and placed in separated containers. The synthesis procedures were demonstrated with the flowchart in Figure 3.1. According to the weight percentage of iron particles (relative to polyol), three types of MFs: MF25-30, MF50-30 and MF75-30 were synthesized at room temperature (25 °C).

Figure 3.1 Flowchart of low density MF synthesis procedures

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According to the weight percentage of iron particles to polyol, three types of MFs: MF25-30, MF50-30 and MF75-30 were produced.

3.3.3 High density MFs (MFXX-55s)

The fabrication procedures of high density MFs were similar to those of low density MFs. The only difference was that a pre-mixing process of the iron particles and polyol was necessary for high density MFs. Due to the heavy loading of iron particles in high density MFs, the foams could not raise properly if the same procedures for the low density MFs were followed. A pre-mixing process was implemented before the conventional synthesis procedure. The parameters such as pre-mixing time, speed and degassing period were investigated and optimized by the author. By applying the pre-mixing process in advance of the mixing and foaming process, the iron particles were distributed evenly and the potential to load more iron particles in MFs increased.

To achieve a more uniform distribution of the iron particle by narrow particle size range, and also to cut down the research cost, iron particles from BASF were applied to replace the iron particles from Sigma Aldrich for the high density MFs. Three types of BASF iron particles – grade EA, ER and HQ, were tested and compared in the foaming synthesis. Grade ER was found to be the optimal selection for the successful synthesis, due to its narrow particle size range.

3.4 Characterization of MFs

3.4.1 Physical properties

i. Colour

The colours of MFs with different iron contents were observed and compared by visual inspection. Pure flexible PU foams are white. Due to the black iron particles, the MFs with higher iron particle loading were supposed to be darker appearance.

ii. Bulk density

The bulk densities of MFs with different iron contents were measured and calculated by applying the formula $\rho = \frac{m}{V}$, where ρ is the bulk density, m is the mass and V is the volume. MFs were cut into regular cubes and cuboids. A weighing balance and a ruler were used to measure the mass and dimension of the MFs respectively.

3.4.2 Morphological properties

i. Stereo-zoom optical microscope

The pore sizes and structures of MF samples were examined through the digital images taken on a stereo-zoom optical microscope (Leica MZ6) at different magnifications.

ii. Scanning electronic microscope (SEM)

The topographical images including the pore sizes, cell wall thickness, and iron particle distribution in the sample surfaces and fractured surfaces were examined under a JEOL SEM. In addition, the elements present in the samples were analyzed using energy dispersive spectroscopy (EDX).

iii. X-ray Computed Tomography (CT)

The inner structure of the MFs and the distribution of the iron particles were determined using 3D X-ray CT scanning. Because the 3D images were reconstructed from 256 2D axial scanned images, a quantitative method was developed to analyse the iron particle distribution based on the 2D axial images of the samples by grouping them into n groups. The details will be given and discussed in section 4.2.2.3 in Chapter 4.

3.4.3 Thermal properties

i. Thermogravimetric Analysis (TGA)

TGA was applied to characterize the thermal degradation properties of the MFXX-30s. The samples of PU-30 and MFXX-30s were cut to an average weight of 10 mg, and tested in TGA 2950 (TA Instrument). TGA curves were obtained at four different heating rates (β) 5 °C/min, 10 °C/min, 20 °C/min, and 40 °C/min, in nitrogen and air environments. The Ozawa and Flynn's method was applied to calculate activation energy from the TGA experimental data in this study [18].

3.4.4 Mechanical properties with a magnetic field

Magnetic sensitivity of the MFs refers to the responsiveness of the mechanical strength with respect to the change of the applied magnetic field. The developed low density and high density MFs were tested on two testing jigs designed by two FYP students (Ang Ann Sheng Justus and Koh Yi Ting) in two academic years, respectively. The MFs were tested under compression loading with vertical magnetic flux and horizontal magnetic flux. The vertical and horizontal testing modes were demonstrated schematically in Figure 3.2 below.

Figure 3.2 Schematic drawing of vertical and horizontal modes of compressive test

i. Vertical mode of compressive test

The low density MF samples were compressed by the iron plunger 1 of the jig 1 connected to the Instron adaptor while the magnetic field was vertical and parallel with the compression direction (Figure 3.3).

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A rate of 60 mm/min was used to compress the foam for a displacement of 10 mm and back to the original position. The test was repeated for 3 cycles for each sample. The measurements were taken at 0, 1.0, and 2.0 Amperes. Tests were made to four MF samples with different iron particle loadings. The samples used in this testing were of 40 mm × 40 mm × 20 mm.

Figure 3.3 Setup of the compressive test in vertical mode of jig 1

The high density MFs were tested with Jig 2, which was an improved version of jig 1. Four more solenoids were added to improve the magnetic field strength. The set up was very similar to the procedure of Jig 1 (Figure 3.4). The only difference was that the sample size was changed to 35 mm × 35 mm × 35 mm cube.

Figure 3.4 Setup of the compressive test in vertical mode of jig 2

ii. Horizontal mode of compressive test

The low density MF samples were tested on Jig 1. In the horizontal mode, an aluminium alloy, plunger 2 was connected to the Instron adaptor to compress the samples while the magnetic field was horizontal and perpendicular to the compression direction (Figure 3.5). Same as the procedure in vertical mode tests, a rate of 60 mm/min was used to compress the foam for a displacement of 10 mm, at 0, 1.0 and 2.0 Amperes. Four MF samples with different iron particle loadings were tested. The sample size used in this testing was 40 mm × 20 mm × 20 mm.

Figure 3.5 Setup of the compressive test in horizontal mode of jig 1

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The high density MFs were tested in Jig 2. The set up was very similar to the procedure of Jig 1 (Figure 3.6). The only difference was that the sample size was changed to 35 mm × 35 mm × 35 mm cube.

Figure 3.6 Setup of the compressive test in horizontal mode of jig 2

3.4.5 Acoustic properties

Measurements of the acoustic parameters of the synthesized magnetic foams were obtained with the use of an impedance tube kit model, based on the two-microphone transfer-function method according to ISO 10534–2 and ASTM E1050–98 international standards. The sound absorption coefficient (SAC) was measured with a two-microphone impedance measurement tube type 4206, to compare the absorption ability of the MFs containing different iron contents in this work. The testing sample size was $\Phi 29\text{mm} \times 25\text{mm}$, and the testing frequency range was 500Hz to 6.4kHz (medium to high frequency range).

3.4.6 Electromagnetic properties

The radar absorption test was conducted in Agilent Network Analyzer N5230A, the measurement of the scattering parameters of 2-port devices. Both low and high density MFs were tested and the testing frequency range was 9 GHz - 11 GHz. The testing sample size was 22.86 mm x 10.16 mm x 50mm.

4. Chapter 4 Results and Discussion

This chapter discusses and analyzes the experimental process and testing results. Section 4.1 describes the development of formulation and synthesis of MFXX-30s and MFXX-55s. Section 4.2 covers the characterization observation and testing of the MFXX-30s.

4.1 MF formulation and process development

The synthesis processes of pure flexible PU foams and low density MFs with low iron contents were relatively simple and straight forward. However, more issues were encountered when the iron particle loading was increased. Some of the typical issues are listed below:

- i. The higher loading of the heavy iron resulted in the poor foam rising during the foaming process.
- ii. More iron particles could disturb the struts of the PU porous structure more and could cause the structure to collapse eventually.
- iii. More iron particles were more difficult to distribute evenly in the foams.

In order to overcome the issues caused by the high iron content loading, the essential chemical components to fabricate the MFs and operation procedures had to be adjusted and modified.

On the other hand, the magnetic sensitivity of MFs was assumed to be proportional to the iron contents. Thus, maximising the iron content loading amount and optimising the magnetic sensitivity of MFs are the major challenges of this project.

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4.1.1 Low density MFs (MFXX-30s)

PU-30 and MF25-30 were synthesized successfully by following the basic formulation. Figure 4.1 illustrates that the smooth cross sections of PU-30 and MF25-30 with uniform cells and crack-free structure. The light grey colour of the MF25-30 was even from top to bottom sections.

Figure 4.1 PU-30 and MF25-30 cross sections

4.1.1.1 Problems encountered

For MF50-30 and MF75-30, the problems found in the synthesized MFs included:

- i. poor rising
- ii. big cracks
- iii. destroyed structure
- iv. uneven distribution of iron particles (SEM observation)

Figures 4.2 – 4.5 below reveal the visual inspection of the failures described above.

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Figure 4.2 Poor rising of MF50-30 and MF75-30

Figure 4.3 Big cracks in MF50-30 and MF75-30

Figure 4.4 Destroyed structure of MF50-30 and MF75-30

Figure 4.5 SEM micrograph of MF75-30, uneven iron particle distribution in the cell walls at 100X magnification

4.1.1.2 Formulation modification

i. Increase in TDI amount

A reason for the poor results might be due to the inappropriate TDI content calculated and added during the synthesis process. It was not noticed that the TDI concentration was actually 80 wt%. Thus a compromising factor during the formulation calculation was necessary to ensure the sufficient TDI amount involved in the main foaming reaction. The added TDI amount was corrected according the equation below:

$$m_{TDI(added)} = \frac{m_{TDI(actual)}}{80\%}$$

ii. Modification of chemical component amounts

The blowing agent (water) causes the foam to expand and rise. Carbon dioxide generated by the reaction between the blowing agent and TDI leads the formation of porous and net-like structure. When the amount of blowing agent was in excess, too many bubbles were generated within a short period of reaction time which might result in cracks in the MFs eventually. Thus, a reduction of blowing agent amount was tested to deal with the problem of big cracks inside

MFs. A reduction of 10 wt% of blowing agent was found to be effective to achieve a crack-free MF structure.

4.1.1.3 Issues Encountered and Improvements in Synthesis Experiments

i. Spillage of TDI during the mixing process

During the synthesis process, after TDI was poured into the cup and mixed in the stirrer unit, large amount of TDI was splashed out of the cup and spattered to the newspapers on the side walls of the fume hood, shown in Figure 4.6 (a). Thus, insufficient amount of TDI was involved in the main reaction of the foaming process.

To overcome this problem, several improvements in the operation procedures were tried and tested. Firstly, the order of the mixing process was changed and the polyol mixture was added into the TDI cup. The consideration was from the viscosity difference of the polyol mixture and the TDI liquid. However, the spillage of TDI was still out of control and this modification was not accepted.

Secondly, the stirrer was turned off after the 30 seconds mixing of the polyol mixture. TDI was added into the polyol mixture cup, and then the stirrer was turned on and slowly increased to the required speed. This modification reduced the possibility of the TDI spillage. However, when TDI and D19 catalyst were added into the polyol mixture cup, spontaneous foaming reactions took place within a few seconds. If the stirrer was turned off and on, then slowly increased to the required speed, reactions would have started before pouring the slurry mixture into the paper box mold. The foam structure of the produced MFs was discontinuous and big cracks were found. Therefore, the attempt was not accepted and the conventional operation procedures were still followed.

The solution to overcome this problem finally was the new “cap” that was designed and fabricated to ensure the minimal spillage of TDI. Figure 4.6 (b) proves the effectiveness of the spillage control of TDI after installing the new cap.

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Figure 4.6 Effectiveness of the new cap to control the TDI spillage, (a) before and (b) after installation of the new cap

ii. Uneven iron particles distribution

As observed in Figure 4.5, the distribution of iron particles in MF75-30 was acceptable but not entirely even on the surface of cell walls. Some of the clusters of iron particles might overload the MF cell walls and speed up the foam structure breakdown after multiple usages. Thus, an even distribution of iron particles was desirable.

One possible reason for the uneven distribution of iron particles might be due to the short time of mixing iron particles with the polyol mixture. A longer mixing time of 120 seconds was used instead of the conventional 30 seconds. The MF75-30s produced under the two conditions were inspected visually and under SEM for their macro and micro structures respectively (Figure 4.7 and 4.8).

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Figure 4.7 Comparison of the macro-structure of the MF75-30s produced by the mixing time of 30 seconds and 120 seconds

Figure 4.8 Comparison of the micro-structures of the MF75-30s produced by the mixing time of 30 seconds and 120 seconds (SEM micrographs at 50X and 100X magnification)

A summary of the comparison of the MFs produced by the two mixing conditions was given in Table 4.1.

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Table 4.1 Comparison of MFs produced by the two mixing conditions

Comparison		Mixing time = 30 s	Mixing time = 120 s
Macro structure	Big cracks	No	Yes
	Bulk volume	Moderate	Large
Micro structure	Cell size	Small, ~200µm	Large, ~ 400µm
	Iron particle distribution	Acceptable	Good

The 120 second mixing condition could achieve a better distribution of iron particle due to the sufficient stirring time. However, too many air bubbles were induced during the process. It explained why large cells were observed under SEM. As a result, large cells and big cracks were formed. The foam structure continuity was disturbed. Thus the 120 second mixing condition was not applicable.

Although a better iron particle distribution may be obtained by increasing the mixing time from the original 30 seconds to 120 seconds, the foam structure was disturbed as a result. Since a stable foam structure is the foundation and basis of foam manufacturing, the conventional mixing time 30 seconds is hence followed, and the mixing time between 30 seconds and 120 seconds were not tested or compared.

4.1.2 High density MFs (MFXX-55s)

The synthesis procedure of high density MFs was more difficult than low density MFs, basically due to two reasons:

- i. High density PU foams require tin catalysts with very narrow processing latitude, which is defined as the range of the acceptable minimum and maximum amounts for stable foam processing. Excess amount of tin catalysts will cause unstable foaming at initial stage, resulting in bottom split. Thus the operation procedures had to be optimized and the accuracy of chemical amounts had to be strictly controlled.

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ii. Thicker cell walls of the high density MFs increased the potential to load more iron particles in the polymeric matrix. This is also our initiative to make high density MFs. As seen in Table 4.2, the weight of iron particles in MF50-55 (88.16 g) was already greater than that in MF75-30 (82.65 g). However, as stated in Section 4.1, the higher iron content, the more difficult it would be to produce successful MFs. Thus, development of high density MFs with high iron particle loading was more challenging than that of low density MFs.

Table 4.2 Iron particle weights of the low and high density MF series

MF types		Polyol weights	Iron particle weights
MFXX-30s	MF25-30	110.2g	27.6g
	MF50-30	110.2g	55.1g
	MF75-30	110.2g	82.7g
MFXX-55s	MF25-55	176.3g	44.1g
	MF50-55	176.3g	88.2g
	MF75-55	176.3g	132.2g

4.1.2.1 Synthesis of MF25-55

The synthesis of MF25-55 was smooth and successful, using both SA iron particles and BASF ER particles. The iron content is not heavy (Table 4.2). Thus the foam rising was proper and the foam structure was flawless. The light grey color was also uniform with eye inspection as showed in Figure 4.9.

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Figure 4.9 Successful MF25-55 with (a) SA particles; and (b) with grade ER iron particles

4.1.2.2 Synthesis of MF50-55

i. SA iron particles

Several tests have been done to fabricate MF50-55(SA) by following the synthesis procedures of the low density MFs. To stabilize the foams structure, silicone surfactant was also increased to 120% ~ 140%. However, either serious shrinkages, or large amount of cell splits were found after the post curing of the foams. Iron particle clusters were found to be at the bottom section, and they did not seem to be embedded in the polymeric matrix. Figures 4.10 – 4.12 displayed the failed MF50-55(SA) bulks.

Figure 4.10 Failed MF50-55(SA) with cell wall fragments and poor rising

Figure 4.11 Failed MF50-55(SA) with vertical shrinkage

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Figure 4.12 Horizontal splits observed on the cross sectional surface of MF50-55(SA)

After consulting a PU foam expert, Mr. Tan Seng Kok from Momentive Performance Materials, a “pre-mixing” of iron particles and polyol method was suggested. Thus, the author did a series of experiments to optimize the crucial parameters in the pre-mixing process. Six samples were produced under different operation conditions (Table 4.3), and examined thru visual inspection and SEM observation. Figure 4.13 are the selected SEM micrographs of the samples.

Table 4.3 Mixing conditions of the pre-mixing samples

MF samples	Mixing contents	Mixing time	Mixing speed	Ultrasonic Degassing	remarks
PM1	Iron + polyol	3.5 hrs	500 rpm	No	
PM2	Iron + polyol	3.5 hrs	250 rpm	No	
PM3	Iron + polyol + L600	3.5 hrs	250 rpm	No	
PM4	Iron + polyol + L600	3.5 hrs	250 rpm	No	
PM5	Iron + polyol + L600	3.5 hrs	250 rpm	Yes	Fail due to process error
PM6	Iron + polyol + L600	3.5 hrs	500 rpm	Yes	

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Figure 4.13 SEM micrographs of MF50-55(SA) samples produced with pre-mixing process

The SEM micrographs of the pre-mixing MF50-55(SA) samples (Figure 4.13) illustrate that the distribution of iron particles in all the samples was significantly improved as compared to the MF75-30 which did not have the pre-mixing process, although MF50-55(SA) had even more iron content than MF75-30 (stated in Table 4.2). The iron particles were fully wetted and wrapped by the viscous polyol liquid during the pre-mixing process, and thus ensured a stable

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embedment of the particles. The 3.5 hour pre-mixing duration provided the sufficient length for a thorough mixing process of the iron particles and polyol. As a result, the particle distribution was generally improved.

The samples produced under the mixing speed of 500 rpm, gave a more even iron particle distribution, as compared with SEM micrographs of PM1 and PM6 to SEM micrographs of PM2, PM3 and PM4 in Figure 4.13. But the faster mixing speed produced more air bubbles which might cause structural problems like big and small cracks. The samples produced under the mixing speed of 250 rpm, had worse particle distribution, but good structure. In order to achieve a good particle distribution, an ultrasonic degassing process was introduced and found to be effective to release the tiny air bubbles out from the liquid mixture (Figure 4.14).

Figure 4.14 Ultrasonic degassing of the mixture of iron particles, polyol and L600

Surfactant L600 was neither evaporable nor sensitive to react with iron particles and polyol. Mixing it thoroughly in the pre-mixing process was assumed to control the cell sizes and to stabilize the produced foam structure. Thus L600 was involved in the pre-mixing process and good structure MF50-55(SA)s were produced.

However, thin membranes were observed in many cell windows, either cover full or half cell windows (e.g. SEM micrograph of PM3 and PM4 in Figure 4.13). Full

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membranes would reduce the connectivity of the open cell structure, while half membranes would not have significant influence to the structure.

ii. BASF ER particles

MF50-55(ER) could not be synthesised based on the original foam formulation. Figure 4.15 below demonstrated small cracks, voids and separating layers at the foam edges. Although the problem of crack and fragmentation still exists, the degree of the defects is of a significantly smaller scale in comparison. Previously, it was proposed that there is a need to revise the formulation. Thus a series of experiments were conducted to investigate the effect of the different recipe components and formulate a possible solution to successful development of MF50-55(ER).

Figure 4.15 Synthesis of MF50-55 using the BASF ER iron particles

1. Adjustments to Tin catalyst, D19

The content of tin catalyst was adjusted to 115% and 130%. With the increased content of D19 at 115% (Figure 4.16 a), although slight cracks are still present in the foam synthesized, there was improvement to the gelling of foam, with an increased resistance to tearing. Tin catalyst D19 in the foam formulation strongly promotes the gelation reaction between the isocyanate and polyol. But with a further increase of D19 to 130% content shown in Figure 4.16 b, the condition of the foam had a drastic change with the formation of a large crack within. The

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condition of the foams synthesized was compromised probably due to the imbalance of the gas evolution reaction, with the concentration of the foam exceeding the optimum level. As such, the exceeding tin catalyst content prevents the relaxation of foam curing due to a tighter polymer matrix as the foam gels faster with a slower expansion of gas bubbles.

Figure 4.16 MF50-55(ER) with adjustments to Tin catalyst content in formulation (a) 115% D19, (b) 130% D19

2. Adjustments to Amine catalysts, Tertiary Amine/Glycol mixture

Figure 4.17 below showed the synthesized MF50-55(ER) with adjustment of the Amine catalysts. The formulation still yields cracks, but during the curing process it is observed that the foams are “blown” to a larger extent with the top surface “overflowing”.

Figure 4.17 MF50-55(ER) with adjustments to Amine catalyst content in formulation (a) increased A33, (b) increased A1

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This can be explained by the existence of the amine catalyst serving as a blowing catalyst in the formulation. After further research on amine catalysts' effect on the formulation of PU foam, it was found that amines offer some contribution to the gelling reaction apart from being blowing catalysts. In the experiments, such condition showed the increased strength of the cell walls with larger resistance when subjected to stretching. On the other hand, the degree of crack formation is higher with increasing amount of amine content. The physical separations (cracks) are most likely due to the motive force of expanding gas bubbles, i.e. higher blowing reaction, exceeding the tensile strength of the polymer matrix.

3. Adjustments to blowing agent, Water

According to the FYP report by the student Cai Xin Lai Lionel [39], the reduction of water content present in the foam resulted in the successful synthesis of MF75-30, with the elimination of the large crack within the foam. Further reduction of water content to 85% was attempted in the experiment. The crack formation was eliminated as predicted but lead to a new defect, the formation of large voids within the foam structure.

Figure 4.18 MF50-55(ER) with reduced water content in the foaming formulation

4. Adjustments to Surfactant, Niaux Silicone L600

The purpose of the silicone surfactant is to lower the surface tension, allowing easier spreading and lowering the interfacial tension during the formation of

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flexible foams. In short, the silicone surfactant stabilises the foam during the curing process. The reduction in silicone L600 content had no significant effect in the experiment, with the defects still present within the foams synthesized without any improvements.

Figure 4.19 MF50-55(ER) with Silicon Surfactant reduction

After careful investigation of the individual chemical components' effect on the condition of the foam synthesized, it was deduced that successful synthesis of MF50-55(ER) was not dependent on the adjustment of a single chemical component but a combination of adjustments to the formulation.

Figure 4.20 Successful synthesis of MF50-55(ER)

Successful synthesis of MF50-55(ER) was developed and replicated in a few experiments with adjustments to the content of the D19 (130%) and amine catalysts (140%); improving the gelation of the cell walls by promoting the gelling reaction with increasing the content of D19 (main) and amine catalysts while

balancing the extent of 'blowing' of polymer matrix during curing with increasing amine content.

4.1.2.3 Synthesis of MF75-55

With the original formulation, the MF750-55(ER) developed shows cracks in regions throughout the foam matrix. With increased weight percentage of iron particles in the formulation, the cell walls are not sufficiently strong enough to hold the iron particles within the polymer matrix. This results in the foam not being able to blow optimally and cell walls collapsed, resulting in crack formation. As such, the foam, as observed in Figure 4.21, has the low height and flat surface due to ineffective 'blowing' during the curing process, forcing the foam matrix to expand horizontally, pushing against the walls of the foam container.

Figure 4.21 Synthesis of MF75-55(ER) with the original formulation

The deduction of insufficient "blowing" was examined and the results, as shown in Figure 4.22a, indicate the improved state of the foam while cracks remained in the foam matrix, stretching across the foam. The second formulation adjustment experiment (Figure 4.22b) is based on the formulation of successful synthesis of MF50-55(ER). As observed, the large crack across the foam remained, although other regions within the foam display the improved gelling of the cell walls with the increased resistance to stretching. The parts of the foam with acceptable structure were cut and used for other testing in the later works.

Figure 4.22 Synthesis of MF75-55(ER), (a) increased amine catalyst, (b) increase D19 and amine catalyst-formulation based on successful synthesis of MF50-55(ER)

4.2 Characterization of MFs

Properties of the low density MFs in five categories i.e. physical, morphological, thermal, mechanical properties with a magnetic field were tested and analyzed after the successful synthesis. The structural, thermal and mechanical properties with a magnetic field were the main concerned aspects and will be discussed in more details.

4.2.1 Physical properties

4.2.1.1 Colour

The similar trend for both low and high density MF series was the colour gradient which could be easily inspected visually. Figure 4.23 demonstrates the cubic samples of PU-30 and MFXX-30s. PU30 was purely white; MF25-30 was light grey; MF50-30 was medium grey and MF75-30 was dark grey. The colour gradient implied for the increment of the iron content from 25 wt% to 75 wt%, for both MFXX-30s and MFXX-55s.

Figure 4.23 Cubic samples of (a). PU30, MF25-30, MF50-30 and MF75-30, in dimension of 50 mm × 50 mm; and (b) PU-55, MF25-55, MF50-55 and MF75-55, in dimension of 35mm × 35mm × 35mm

4.2.1.2 Bulk density

The estimated bulk density of the base PU foam was 30 Kg/m³ according to the formulation, and the actual average bulk density was measured as 32.6 Kg/m³. The estimated bulk density of PU-55 was 55 Kg/m³, and the actual average bulk density of the synthesized PU-55 was 52.5 Kg/m³. Table 4.4 provides the bulk density results and Figure 4.24 shows the relationship between the foam bulk density and iron content. As the iron content was increased, a linear relationship of bulk density and iron content was observed for both low and high density foams. Since the volume was assumed to be constant for each MF bulk, MF density was supposed to increase linearly with the iron content.

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Table 4.4 Experimental data for calculation of bulk density of MFXX-30s

MF type		Bulk density (Kg/m ³)					
		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Average ρ_{bulk}
MFXX-30s	PU-30	31.7	33.2	32.9	-	-	32.6
	MF25-30	37.7	38.4	38.0	37.0	38.7	38.0
	MF50-30	43.4	42.6	43.9	-	-	43.3
	MF75-30	51.2	51.3	50.7	51.7	52.1	51.4
MFXX-55s	PU-55	52.7	52.5	52.5	-	-	52.5
	MF25-55	58.2	59.5	59.5	-	-	59.5
	MF50-55	67.1	66.4	66.4	-	-	66.4
	MF75-55	76.4	77.7	77.7	-	-	77.7

Figure 4.24 Bulk density of MFXX30s and MFXX-55s

4.2.2 Morphological properties

4.2.2.1 Stereo-zoom optical micrographs

Stereo-zoom optical micrographs in Figure 4.25 illustrate a typical cellular structure of the flexible foams. The cell diameter varies from 0.2mm to 0.5mm.

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There were no significant influences on the cell structure after carbonyl iron particles were added for MF25-30, MF50-30 and MF75-30, except that the colour became darker as the iron content was increased. An open cell structure was observed for the four compositions, which implied a good connectivity of the pores and adequate thermal conductivity of the flexible magnetic foams.

Figure 4.25 Stereo-zoom optical micrographs of MFX-30s

4.2.2.2 SEM micrographs

SEM micrographs provide more information about the morphology and iron particle distribution. Figure 4.26 shows the SEM micrographs of PU-30 and low density MFs, while Figure 4. 27 does the SEM micrographs of PU-55 and high density MFs.

Figure 4.26 (a) illustrates clear and smooth cell walls of PU-30, with an average pore size about 260 μ m. Figure 4.26 (b) illustrates MF25-30, with a pore size about 300 μ m and cell wall thickness about 100 μ m. Iron particles were observed

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as the white spherical shape under the Backscattered Electron Image (BEI) mode. For MF50-30 and MF75-30, the pore size and cell wall thickness did not show any significant changes. Due to the increased iron particle content, the crowded but adequate distribution of iron particles within the cell walls was seen in Figure 4.26 (c) and (d). The distribution was not perfectly uniform, because of the limited mixing time of the particles. Figure 4.26 (e) presented the cell wall surface with fully embedded iron particles. Figure 4.26(f) revealed the cross section surface of a cell wall of the magnetic foams. The spherical iron particles were observed to be half-embedded in the polymeric matrix.

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Figure 4.26 SEM micrographs of PU-30 and MFXX-30s: (a) PU-30, (b) MF25-30, (c) MF50-30, (d) MF75-30, (e) cell wall surface, (f) cell wall cross section

Figure 4.27 SEM micrographs of PU-55 and MFXX-55s: (a) PU-55, (b) MF25-55, (c) MF50-55, (d) MF75-55

Similarly, Figure 4.27 illustrates the network structure and the iron particle distribution in high density MFs. Table 4.5 lists the measured pore size and cell wall thickness of the low and high density PU and MFs. The calculated data

proves that the high density PU and MFs have apparently smaller pore sizes and larger cell wall thickness than low density PU and MFs.

Table 4.5 Pore size and the cell wall thickness of low and high density PU and MFs

MF type	Pore size		Cell wall thickness	
PU-30	~280 μm	Average: ~300 μm	~70 μm	Average: ~95 μm
MF25-30	~300 μm		~100 μm	
MF50-30	~300 μm		~110 μm	
MF75-30	~310 μm		~100 μm	
PU-55	~230 μm	Average: ~250 μm	~180 μm	Average: ~160 μm
MF25-55	~230 μm		~140 μm	
MF50-55	~280 μm		~170 μm	
MF75-55	~260 μm		~150 μm	

The iron particle distribution in high density MFs were not as uniform as shown in low density MFs. There were agglomerates observed in MF50-55 and MF75-55 cell surfaces.

4.2.2.3 X-ray Computed Tomography

Figure 4.28 presents the reconstruction 3D CT images of the low and high density MFs. Internal network structures of the MFs were observed. Due to the different X-ray absorption ability of metal and polymer, the iron particles are reflected as white colour in the images, and the PU polymer is not visible in the image. For both low and high density MFs, the MFs with more iron content gave denser look in the 3D images. The results showed the significant differences between the MFs with different iron contents. The high density MFs appeared generally denser than low density MFs.

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Figure 4.28 Reconstructed 3D CT images of MFXX-30s (a, b, c) and MFXX-55s (d, e, f)

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The 3D CT images were reconstructed from the 256 2D axial images in 360 degree rotation. The 2D axial image of the low and high density MFs may give better details for analysis, demonstrated in Figure 4.29. The net-working white portions are the polymer struts that were occupied by the iron particles. Similarly the clearance and the density of the networks increased with the iron contents for both low and high density MFs. It could also be seen that for some samples, the white noise circles were quite obvious (Figure 4.29 c).

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Figure 4.29 Axial CT images of MFXX-30s (a, b, c) and MFXX-55s (d, e, f)

The detailed procedures of the quantitative analysis of the iron particle distribution are as follows and schematically illustrated in Figure 4.30:

For all the samples:

1. Determine sampling size x (around 200 to 270 2D axial images) for each sample
2. Divide sample into n groups. In this experiment, $n = 8$

For each image:

3. Convert the grey scale image to a binary-level image
4. Calculate the area covered with iron particles by counting the number of white pixels in the image
5. Calculate percentage of iron particles (white area) with respect to the sample cross-section area in each image

For each group:

6. Derive the average percentage of iron particles for each group
7. Plot graph of the average percentages of the 10 groups for each sample

Figure 4.30 Schematic drawing of the quantitative analysis of the iron particle distribution

Several difficulties were faced in the process of obtaining the CT results. Firstly, bright circle noise was generated by the container (Figure 4.29 c). This issue occurred only in segments of the results. Furthermore, the images were also taken at different levels of light intensity (Figure 4.29 c and f).

To overcome the abovementioned problems, each segment have its own optimum threshold. Each segment is examined for the bright circle noise and its overall light intensity, and then the threshold is adjusted accordingly.

Table 4.6 tabulated the experimental calculated iron content of the 8 segments for the low and high density MFs according to the binary CT 2D axial graphs and Figure 4.31 plotted the data. From Figure 4.31 the distribution of the iron particles was relatively even for each MF in different segments. This meant that the iron particle distribution is relatively even throughout the entire foam samples. The distribution for the high density MFs were slightly fluctuating in different segments. It implied that the iron particle distribution in high density MFs was less even than that in low density MFs. The experimental volume percentage of the iron content in all the MFs are relatively in proportion, e.g. MF25-30 had the lowest values and the MF75-55 had the highest values.

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Table 4.6 Experimental calculated volume percentage of iron particles in MFXX-30s and MFXX-55s

MF type		Iron volume percentage in segments (%)								Average (%)
		1	2	3	4	5	6	7	8	
MFXX-30s	MF25-30	0.45	0.47	0.53	0.46	0.57	1.11	0.81	0.73	0.64
	MF50-30	1.45	1.52	1.37	1.60	1.56	1.76	1.78	1.65	1.59
	MF75-30	1.79	2.07	1.86	2.00	2.26	2.24	2.12	2.25	2.08
MFXX-55s	MF25-55	1.55	1.25	1.49	1.93	2.03	1.72	1.3	1.07	1.54
	MF50-55	2.33	2.50	2.95	3.31	3.19	2.69	2.35	2.41	2.72
	MF75-55	3.07	3.08	3.44	3.59	3.49	3.16	3.09	3.22	3.27

Figure 4.31 Experimental calculated volume percentage of iron particles MFXX-30s and MFXX-55s

The theoretical estimated volume percentage of the iron particles in all MFs was calculated and tabulated in Table 4.7. The calculation procedure of MF25-30 was illustrated below:

$$\frac{V_{Fe}}{V_{foam}} = \frac{m_{Fe} / \rho_{Fe}}{V_{foam}} = \frac{27.5 \times 10^{-3} \text{ kg} / 4400 \text{ kg/m}^3}{0.18 \text{ m} \times 0.18 \text{ m} \times 0.09 \text{ m}} = 0.0021 = 0.21\%$$

Table 4.7 Theoretical estimated volume percentage of iron particles in MFXX-30s and MFXX-55s

MF type		Iron particle weights (g)	Iron volume percentage (%)
MFXX-30s	MF25-30	27.5	0.21
	MF50-30	55.1	0.43
	MF75-30	82.7	0.64
MFXX-55s	MF25-55	44.1	0.34
	MF50-55	88.2	0.68
	MF75-55	132.2	1.03

Comparing the theoretical (Table 4.7) and experimental data (Table 4.6) of the iron volume percentage, the experimental results were apparently larger than the theoretical estimation, around three times larger. The most possible reason was due to the resolution limitation of the equipment. The average carbonyl iron particle size was 5 μm, which is smaller than the maximum equipment resolution of 10 μm. Moreover the image noise and signal loss in the binary conversion also contributed to the error. However the distribution in different portions/groups of each sample and the comparison of different samples were still meaningful and useful. With this 3D structural analysis, the low and high density MFs were deemed to posses acceptable iron distribution. The low density MFs generally have better distribution than the high density MFs.

4.2.3 Thermal properties

4.2.3.1 TGA

i. Thermogravimetric analysis

Figures 32 and 33 illustrate the thermogravimetric (TG) and differential TG (DTG) curves for the low and high density foams in nitrogen and air at a heating rate of 5 °C/min respectively. The onset temperature (T_{on}) is defined as the temperature when the start of weight loss, which can be determined from the onset point of the DTG curves, as shown in Figure 4.32 a. The TG characteristic data such as T_{on} , the peak temperature (T_{max}) at each degradation stage from the DTG curves and the residual percentage at 600 °C from the TG curves are given in Table 4.8 and 4.9.

Figure 4.32 (a) TG and DTG curves of PU-30 and MFXX-30s in nitrogen, at a heating rate of 5°C/min; (b) TG and DTG curves of PU-55 and MFXX-55s in nitrogen, at a heating rate of 5°C/min

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Figure 4.33 (a) TG and DTG curves of PU-30 and MFXX-30s in air at a heating rate of 5°C/min; (b) TG and DTG curves of PU-55 and MFXX-55s in air at a heating rate of 5°C/min

Table 4.8 parameters for PU-30 and MFXX-30s in nitrogen (10°C/min) and air (5°C/min)

	Sample	Stage 1		Stage 2		10 wt% loss temperature (°C)	50 wt% loss temperature (°C)	Residue at 600 °C (%)	Actual iron percentage (%)*
		T _{1on} (°C)	T _{1max} (°C)	T _{2on} (°C)	T _{2max} (°C)				
N ₂	PU-30	232.0	294.6	324.6	374.0	266.2	350.9	0	0
	MF25-30	228.6	285.2	313.6	373.5	260.1	348.4	16.1	14.3
	MF50-30	213.5	282.6	303.3	367.4	260.7	356.6	25.6	25.0

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	MF75-30	224.8	285.8	313.5	371.9	266.6	363.8	33.9	33.3
Air	PU-30	233.1	295.6	288.3	329.0	257.5	285.8	0	0
	MF25-30	225.8	271.9	283.3	289.2	257.3	285.8	20.2	14.3
	MF50-30	219.2	267.8	275.4	282.1	253.2	283.9	35.1	25.0
	MF75-30	218.3	266.9	274.3	281.1	253.6	288.3	47.1	33.3

* calculated from the formula (iron weight) / (weight of all components in foams).

Table 4.9 TGA parameters for PU-55 and MFXX-30s in nitrogen and air (5 °C/min)

	Sample	Stage 1		Stage 2		Stage 3		10 wt% loss temperature (°C)	50 wt% loss temperature (°C)	Residue at 600 °C (%)	Actual iron percentage (%)*
		T _{1on} (°C)	T _{1max} (°C)	T _{2on} (°C)	T _{2max} (°C)	T _{3on} (°C)	T _{3max} (°C)				
N ₂	PU-55	231.2	274.2	310.7	355.8	-	-	256.9	344.6	0	0
	MF25-55	225.8	273.1	313.2	356.9	-	-	257.3	350.0	15.0	15.3
	MF50-55	220.5	267.4	311.4	349.5	-	-	257.5	349.6	27.9	26.5
	MF75-55	217.7	269.3	312.1	353.9	-	-	261.8	358.0	36.8	35.1
Air	PU-55	237.9	263.5	270.6	299.7	313.5	360.5	250.8	287.5	0	0
	MF25-55	232.4	258.7	268.2	295.2	305.3	246.1	248.0	296.4	19.9	15.3
	MF50-55	223.8	257.1	-	-	-	-	242.0	280.4	38.2	26.5
	MF75-55	223.7	240.7	-	-	-	-	237.4	287.3	51.0	35.1

* calculated from the formula (iron weight) / (weight of all components in foams).

The TG and DTG curves of the PU and MFs obtained in nitrogen display two distinct degradation stages (Figure 32). The magnitudes of the two peaks in DTG were obtained, representing the maximum weight loss rates at the two stages. The two-stage degradation behavior was consistent with the results obtained by other researchers [40, 41, 42]. According to the literature [43, 44], the weight loss

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at the initial stage was due to the degradation of hard segments, isocyanate (TDI) and the second-stage degradation was associated to the soft segments, polyol (PPG). Grassie and Zulfiqar proposed the formation of carbodiimide from the thermally decomposed isocyanates during the degradation process [45]:

In addition, volatile polyureas may be formed by reaction between isocyanates and amines. As a result, isocyanates are evolved in the relatively low temperature range and released as a product termed “yellow smoke”. After the decomposition of the hard-segment isocyanates, the left liquid state polyol is responsible for the molten burning characteristics of flexible PU foam [46]. This explained why the hard-segment isocyanate degraded at the first stage and the soft-segments polyol degraded at the second stage.

Figure 4.32 demonstrates the significant shift of the TG curves to higher temperature with increasing the iron content in the MFs. The weight loss at a given temperature from the TG curves and the weight loss rates at the two degradation stages from the DTG curves decreased in the order: PU-55 > MF25-55 > MF50-55 > MF75-55. The results indicate that the iron particles delayed or suppressed the thermal degradation of the MFs in nitrogen. The iron particles are inert in nitrogen. During the degradation of PU, the iron particles may act as fillers to restrict the PU molecular chain motion upon heating and thus delay the thermal degradation of MFs.

The degradation behaviours of the MFs in air are much different from those in nitrogen. As shown in Figure 4.33 a, the degradation two stages of PU-30 and MFXX-30s in air were not as obvious as in nitrogen. For PU-55 and MFXX-55s, a three-stage degradation behaviour was shown for PU-55 and MF25-55, while a weak two-stage degradation behaviour was observed for MF50-55 and MF75-55 (Figure 4.33 b). The DTG curves revealed the complexity of the oxygen-involved degradation, which included not only the oxidation of polyurethane but also the oxidation of the iron particles and even the metal-polymer interaction during the oxidative decomposition [47, 48].

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The extracted initial 10 wt% and 50 wt% loss temperatures of the foams in nitrogen and air are plotted in Figure 4.34. The 10 wt% loss and 50 wt% loss temperature in nitrogen increased slightly with increasing the iron content, suggesting a stabilizing effect caused by the iron particles in the MFs.

Figure 4.34 Temperature at 10 wt% loss and 50 wt% loss of (a) PU-30 and MFXX-30s; (b) PU-55 and MFXX-55s in nitrogen and air, at a heating rate of 5°C/min

In Figure 4.34, for both of the low and high density foams, the lowest temperatures were observed at 10 wt% loss for the MFs in air. The more the iron content, the lower the 10 wt% loss temperature. However, the 50 wt% loss temperature in air did not show such a trend, but varied with the iron content,

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indicating that the oxygen-involved degradation was much more complicated than that in nitrogen. Generally, the 10 wt% loss and 50 wt% loss temperatures were higher in nitrogen than the corresponding temperatures in air for all the foams. The difference in temperature between nitrogen and air was not large at the initial 10 wt% loss, but became very large at the 50 wt% loss, indicating the different degradation mechanisms involved in the two environments.

Upon heating, the degradation of MFs started from the PU strut where the iron particles were embedded or wrapped. The oxidative degradation of the PU was dominating at the initial stage. Thus the degradations PU-55 and MF25-55 were fast at the initial stage with high weight loss rates and gradually became slower. With more iron particles, the well dispersed iron particles in MF50-55 and MF75-55 separated the polymer struts into smaller regions and increased the surface area for the oxidation reactions. According to Tannenbaum et al [47] the interaction between the metal and the polymer might occur after the formation of the metal oxide clusters. Metal oxide clusters, as the main product of the metal carbonyl decomposition, could provide large surface areas for their reactions with the matrix polymer. In addition, Kalnin et al and Day et al also suggested that metal (copper, steel, iron oxide) could have a catalytic effect on the degradation process of polymers such as polyethylene, polypropylene, polyurethane, poly(vinyl chloride) and acrylonitrile butadiene styrene (ABS) [49, 50]. Even though the mechanism for the oxygen-involved thermal degradation of the MFs has not been fully understood in this study, it is important to know the fact that the iron particles lowered the 10 wt% loss degradation temperature and quickened the thermal degradation of the MFs in air.

The actual iron content percentages in the MFs, which were calculated by the formula of iron weight / total weight of all the components, are given in Table 4.8 and 4.9. The iron residue percentages at 600 °C are also shown in Table 4.8 and 4.9. The iron residue percentages of the MFs in nitrogen were verifiable with the actual ones, while the residue percentages in air were significantly larger than the actual ones. Figure 4.33 shows that the residue weights of the MFs slightly rise up after 400 °C. It is believed that the iron oxides formed in the oxidative

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reactions caused the increase in the residue weights during and after the degradation process [47].

ii. Degradation kinetic analysis

Activation energy is one of the important parameters to characterize the thermal degradation kinetics. There were a few popular analytical methods for calculating the apparent activation energy of degradation from the TG experimental data, e.g. Ozawa, Flynn, Kissinger, Van Krevelen, etc [51, 52, 53]. The apparent activation energy determined from the experimental TG data is strongly dependent on the applied method, and the degree of conversion [43].

Figure 4.35 TG curves of MF75-55 in (a) nitrogen and (b) air, at four different heating rates, 0.5 to 40 °C/min

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Figure 4.35 demonstrates the TG curves for one sample (MF75-55) at four different heating rates (5, 10, 20 and 40 °C/min) in nitrogen and air. The TG curves shift to the left (i.e. higher temperature) with increasing heating rate in a good order. This phenomenon is known to be the time-dependent properties of polymers. A higher heating rate would give a shorter time to the polymer to “react” with the temperature change, so leading to a resisting and delaying effect on the degradation.

In this study, the Ozawa's method was applied to calculate the apparent activation energy [52, 56]. The TG curves for one sample at four different heating rates (β) were required (Figure 4.35) and temperatures at various degrees of conversion (α) were extracted from the TG curves. The degree of conversion is defined as:

$$\alpha = 1 - w(t) / w_0 \quad (\text{Equation 4.2})$$

where w_0 and $w(t)$ are the initial weight and the weight at time t [53]. It also refers to the reaction rate in the thermogravimetric analysis.

By plotting $\ln \beta$ against $1000/T$, the apparent activation energy (E_a) could be calculated from the slope of the linear relationship at each degree of conversion:

$$E_a = -\frac{R \cdot \text{slope}}{1.052} \text{ (kJ/mol)} \quad (\text{Equation 4.3})$$

where R is the universal gas constant.

Figure 4.36 illustrates the relationships between $\ln \beta$ and $1000/T$ for MF75-55 at 10 different degrees of conversion from 5 % to 50 % in nitrogen and air. According to Equation 4.3, the slope of each straight line could give an apparent activation energy at the corresponding degree of conversion. Table 3 lists the calculated apparent activation energy and correlation coefficient (r^2) for MF75-55. The apparent activation energies for the pure PU foams and MFs in both nitrogen and air are plotted against the degree of conversion in Figure 4.37 and 4.38.

Figure 4.36 $\ln \beta$ versus $1000/T$ for MF75-55: (a) in nitrogen and (b) air

Table 4.10 Activation energy and correlation coefficient for MF75-55

α , %	Nitrogen		Air	
	E_a (kJ/mol)	r^2	E_a (kJ/mol)	r^2
5	191.6	0.9947	186.5	0.956
10	178.4	0.997	163.4	0.966
15	167.8	0.998	152.0	0.969
20	156.0	0.988	150.0	0.969
25	181.7	0.967	153.7	0.974

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30	190.9	0.966	159.9	0.984
35	195.8	0.969	169.6	0.995
40	199.3	0.972	177.7	0.999
45	202.6	0.975	184.9417	0.9991
50	205.5	0.978	214.9	0.995

Figures 4.37 and 4.38 illustrated the apparent activation energies of the low and high density foams, respectively. In Figure 4.37 a, the apparent activation energies at different degrees of conversion (5 % - 50 %) in nitrogen were relatively high and stable except a minimum value in the α range around 25 % to 35 %. This minimum value represents the most active moment in the degradation reactions. The activation energy varied in the range from 118 to 221 kJ/mol. The MFs showed the higher activation energies than that of PU-55 along the range of the degree of conversion, except MF75-55 that exhibited the lower activation energy at higher degree of conversion (30 % - 50 %).

The apparent activation energies in air shown in Figure 4.37 b varied in the range from 118 to 261 kJ/mol. The effects of iron content on the activation energy in air were also more significant than those in nitrogen. It was interesting to note that the effects of iron content on the activation energy were different at low and high degrees of conversion or weight loss percentage. At low degrees of conversion (approximately < 30%), the pure PU showed the highest E_a , followed by MF25-55, MF50-55 and MF75-55 in a good order, implying that E_a decreased with increasing the iron content. After undergoing a transition region in the vicinity of 35% weight loss, the effects of iron content on E_a turned in an opposite way at high weigh loss percentages (approximately > 35%): E_a increased with increasing the iron content, [except the two values of MF50-30 and MF75-30 at 40 % and 45 %]. In Figure 4.37 b, all the E_a curves did not show an apparent valley at the mediate weigh loss percentages as observed in Figure 4.37 a. The common point in Figures 4.37 a and 4.37 b was that MF75-30 always showed the highest E_a at high degree of conversion or weight loss percentages.

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Figure 4.37 Apparent activation energy of PU-30 and MFXX-30s at different degrees of conversion: (a) in nitrogen and (b) in air

Figure 4.38 Apparent activation energy of PU-55 and MFXX-55s at different degrees of conversion: (a) in nitrogen and (b) in air

The general pattern of the apparent activation energies of the high density foams were very similar to those of the low density foams. As observed in Figure 4.38 a, the apparent activation energies of the higher density foams exhibited a minimum value in the α range around 20 % to 25 %, slightly earlier than low density foams. The activation energy varied in the range from 137 to 206 kJ/mol. At the initial degradation stage, the MFs showed higher activation energies than that of PU-55. With increasing α , the activation energy of the MFs became lower than that of PU-55, except MF75-55 that exhibited the highest activation energy outstandingly.

The apparent activation energies in air shown in Figure 4.38 b varied in the range from 110 to 217 kJ/mol. The effects of iron content on the activation energy in air were also more significant than those in nitrogen. Similar to low density foams, the iron content showed different effects on the activation energy at low and high

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α . At low degrees of conversion (approximately $< 27\%$), [except one point at 5% weight loss for MF25-55] the pure PU showed the highest E_a , followed by MF25-55, MF50-55 and MF75-55, implying that E_a decreased with increasing the iron content. After undergoing a transition region in the vicinity of 30% weight loss, the effects of iron content on E_a turned in an opposite way at high weight loss percentages (approximately $> 33\%$): E_a increased with increasing the iron content. In Figure 4.38 b, all the E_a curves did not show an apparent valley at the medium weight loss percentages as observed in Figure 4.38 a. The common point in Figures 4.38 a and 4.38 b was that MF75-55 always showed the highest E_a at high α .

Comparing Figures 4.37 b and 4.38 b, when low and high density foams degraded in air, the general pattern for the effect of iron particles was that the activation energy decreased as the iron content increased at the initial degradation stage, indicating a reduced thermal stability by the presence of iron particles in the MFs. However, the activation energy of PU-30 and PU-55 decreased monotonously with increasing α while MF25-30, MF25-55 and MF50-55 exhibited a weaker dependence of E_a on α . MF50-30, MF75-30 and MF75-55 even increased with increasing α . This result might suggest that the iron particles weakened the PU matrix at the early stage of degradation but tended to stabilize the partially degraded matrix at the later stage of degradation by forming the metal-polymer complexes in the presence of oxygen.

4.2.4 Mechanical properties with a magnetic field

4.2.4.1 Compressive test in the vertical mode

The compressive stress-strain curves at the current values of 0, 1.0 and 2.0 A for the low and high density foams were plotted in Figures 4.39 and 4.40. The 1st cycle for each case was excluded due to the significantly higher stress value. The 2nd and 3rd curves were of more concern and are discussed in this section [54, 55].

Figures 4.39 and 4.40 revealed a consistent trend for the low and high density MFs that the compressive stress decreased with increasing current or magnetic

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field. There was no distinct influence in the stress-strain curves but the minute decreasing trend in the applied compressive stress was observed and could be explained as follows.

Figure 4.39 Compressive stress-strain curves for PU-30 and MFXX-30s in the vertical mode (VM) of compressive test, at 60 mm/min for 3 cycles at room temperature

Figure 4.40 Compressive stress-strain curves for PU-55 and MFXX-55s in the vertical mode (VM) of compressive test, at 60 mm/min for 3 cycles at room temperature

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Under a vertical magnetic field, the iron particles would be redistributed in the deformed polymeric cell walls, which might cause a compressive internal stress in the vertical direction. The vertical attraction of the iron particles would result in slight height shrinkage. Based on the assumption of the constant bulk volume of the MFs, a horizontal expansion would take place. The phenomenon is schematically illustrated in Figure 4.41.

Figure 4.41 Effect of vertical magnetic flux on MFs in compressive test

The total compressive displacement was a constant set in the test profile. The relationship of the total and actual compressive displacement is expressed by the formula below:

$$l_{TOT} = l_{ACT} + \Delta l = \text{constant},$$

where l_{TOT} is the total compressive displacement, l_{ACT} is the actual compressive displacement, and Δl is the height decrement produced by vertical iron particle attraction under the magnetic field but not necessarily a constant during the compressive process.

Increasing current would produce a larger magnetic field strength. The stronger attraction of the iron particles would increase the height decrement Δl . Due to the constant total compressive displacement l_{TOT} , the actual compressive displacement l_{ACT} would decrease when the height decrement Δl increases. A larger stress is required for a larger actual compressive displacement l_{ACT} . This explains the minute decrease in the measured stress when current was increased in the vertical mode of compressive test.

4.2.4.2 Compressive test in the horizontal mode

Figures 4.42 and 4.43 present the compressive stress-strain curves at the current values of 0, 1.0 and 2.0 A for the low and high density foams in the horizontal mode compressive test. The representative 2nd and 3rd curves were plotted and compared for different current values.

Again, the difference between the stress-strain curves of different current values was not significant, although a minute increasing trend of the compressive stress with increasing current was found in the low and high density MFs. The possible reason was explained as follows.

Under the horizontal magnetic field, a height increment of the MF bulk could take place when there was a width shrinkage produced by the iron particle attraction, assuming the bulk volume of the MFs was constant. The phenomenon is schematically shown in Figure 4.44.

Figure 4.42 Effects of horizontal magnetic flux on MFs in compressive test

The formula below gives the relationship of total and the actual compressive displacement of the MFs:

$$l_{TOT} = l_{ACT} - \Delta l = \text{constant},$$

where l_{TOT} is the controlled total compressive displacement, l_{ACT} is the actual compressive displacement, and Δl is the height increment produced by horizontal iron particle attraction under the magnetic field but not necessarily a constant during the compressive process.

An increment of current from 0 to 2.0 A would produce a largely increased magnetic field strength. The stronger attraction of the iron particles would increase the height increment Δl . Due to the constant total compressive displacement l_{TOT} , the actual compressive displacement l_{ACT} would increase

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when the height increment Δl increases. More actual displacement would result in larger measured stress. This might explain the minute increase in the applied stress when current was increased in the horizontal mode of compressive test.

Figure 4.43 Compressive stress-strain curves for PU-30 and MFXX-30s in the horizontal mode (HM) of compressive test, at 60 mm/min for 3 cycles at room temperature

Figure 4.44 Compressive stress-strain curves for PU-55 and MFXX-55s in the horizontal mode (HM) of compressive test, at 60 mm/min for 3 cycles at room temperature

4.2.4.3 Summary

The experimental results obtained from the compressive tests for the PU-30 and MFXX-30s show that the sensitivity of the MFXX-30s responding to the external magnetic field was not outstanding at the current stage. It could hardly differentiate the effects of the iron content in different MFs on the mechanical properties under a magnetic field.

As the three dimensional structure of the PU foams is composed of large volume of air voids and thin PU struts, low volumetric density of the iron particles in the MFs was presumed to be one of the reasons for the insensitive response of MFs to the magnetic field. Another possible reason was the restriction of the iron particles by the cured solid PU polymeric matrix. Unlike MR fluids, the iron particles are unable to flow freely to form the chain-like structures. Thus the induced magnetic attraction between the iron particles in the MFs was too weak to respond to the applied magnetic field. Further development in higher density MFs are demanded for a potential sensitive MR effect.

4.2.5 Sound Absorption Properties

The sound absorption coefficient (SAC) of the low and high density foams in the frequency range of 500 – 6400 Hz were tested and plotted in Figure 4.45.

It was found that the SAC for PU foams and MFs were frequency-dependent over the tested frequency range. The general characteristics of the SAC curves were very similar for all the PU and magnetic foams. The SAC magnitude increased almost linearly from 500Hz to certain frequency to reach a peak. The peak magnitude then gradually decreased slightly to form a valley in the middle frequency range and finally raised a bit in the high frequency range. The peak SAC magnitude and corresponding frequency were extracted and tabulated in Table 4.11.

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Figure 4.45 SAC curves of (a) the low and (b) the high density MFs

Table 4.11 Extracted data from SAC curves for the low and high density foams

MF type		Peak SAC magnitude (%)	Frequency at peak SAC magnitude (Hz)
PU-30		76%	3700
MFXX-30s	MF25-30	90%	3000
	MF50-30	95%	2860
	MF75-30	99.5%	2100

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PU-55		66%	1200
MFXX-55s	MF25-55	99.8%	1760
	MF50-55	99.7%	1500
	MF75-55	80%	950

The SAC magnitude of PU-30 grew gradually with increasing frequency. It reached its peak magnitude of 76% at the frequency of 3700 Hz. The SAC magnitude only dropped a little bit and mostly maintained at around 70% in the high frequency range. From MF 25-30 to MF75-30, the peak SAC magnitude increased, and the corresponding frequency shifted to lower values accordingly. The slopes of the SAC curves also increased with increasing iron contents. Generally MFXX-30s showed higher SAC magnitudes over the tested frequency range than PU-30, and the general SAC magnitudes increased with the iron content. MF75-30 even showed almost 100% SAC at 2100Hz. This may imply that the iron content seemed to improve the sound absorption ability of the PU foams. Moreover, MFXX-30s reached the local peak SAC magnitudes earlier than PU-30, which meant that it broaden the frequency range (especially lower range from 500 Hz to 2000 Hz) to be applied to the magnetic foams. PU-30 gave a more flatten SAC magnitude over the higher frequency range, MFXX-30s showed more fluctuating characteristics.

The SAC curves for MFXX-55s were more complicated than MFXX-30s. after increasing the bulk density, PU-55 showed slightly different SAC characteristics from PU-30. It reached the peak SAC magnitude of 66% at approximately 1200 Hz. It was much lower than the frequency for MF-30 to reach the peak SAC magnitude, which was around 3700 Hz. This peak value only lasted in a short frequency range, then it quickly went to a valley range until it rose again and kept the SAC magnitude of 65% from 3000 Hz till 6400 Hz. The SAC curves for MF25-55 and MF50-55 were quite similar and they both had almost 100% high peak SAC magnitude. The main difference was that the SAC curve of MF50-55 shifted the frequency of the peak magnitude slightly from MF25-55. The frequency of the peak SAC magnitude for MF25-55 was 1760 Hz and 1500 Hz, respectively. The

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SAC curve for MF75-55 further shifted the frequency of the peak SAC magnitude to 950 Hz. The peak SAC magnitude dropped to 80%, then rose and maintained at around 82% over the higher frequency range. However, it still could be concluded that the SAC magnitudes of MFXX-55s were generally higher than PU-55, and the frequency of the peak SAC magnitude for MFXX-55s decreased with increasing iron content.

There are two main mechanisms of the sound absorption for porous absorbers. Both of the two mechanisms convert the sound energy into heat energy, through the air flow and thermal conduction. Generally, the magnetic foams allowed air to flow into the cellular structure where sound energy was converted into heat. Initially, there was viscous loss as air was pumped into and out of the open porous structures. There was also damping of the foam structures. Damping refers to the capacity of the material to dissipate energy.

Flexible PU foam themselves were good sound absorbers due to the open-cell porous structure. With the carbonyl iron particles incorporated, any shifting or influences to the SAC characteristics were meaningful. For both low and high density MFs, the SAC magnitudes were generally higher than the pure PU foams.

The developed MFXX-55s with the BASF iron generally have larger slopes for the SAC curves at low frequency range than the MFXX-30s with SA iron. It implied that the developed MFXX-55s could sufficiently absorb more lower frequency sounds, and applied in wider ranges of frequency than the developed MFXX-30s. Thus the developed MFXX-55s were very suitable for the applications of the low and mid-range frequency noise absorption, e.g. office machinery, circular saws, human voice. In summary, the carbonyl iron content in the low and high density MFs had significant influences on the sound absorption ability.

4.2.6 Radar Absorption Properties

The testing and analytical method for radar absorption properties of the magnetic foams was to generalize the scattering matrix and mode-matching from a 2-port device.

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Figure 4.46 shows how the radar signal interacted with the magnetic foam sample. The parameter l is the length of the foam block. A_1^+ and A_2^- are unknown coefficients of the incident electromagnetic waves from the waveguide port, while A_1^- and A_2^+ are the unknown coefficients of the reflected waves. A_d^+ and A_d^- are the unknown coefficients of the forward and backward electromagnetic waves inside the foam sample.

Figure 4.46 Schematic interaction between the radar signal and the sample magnetic foam

The propagation constant γ was defined as: $\gamma = \sqrt{\left(\frac{2\pi}{a}\right)^2 - k_0^2 \mu_r \epsilon_r}$, where k_0 is the wave number in free space; μ_r is the complex permeability; ϵ_r is the complex permittivity. And the signal propagation on the length of uniform transmission line L was defined as: $L = e^{-\gamma l}$.

Matching the tangential fields at left boundary, we could obtain the following two equations:

$$\begin{aligned} A_1^+ + A_1^- &= A_d^+ + A_d^- \\ A_1^+ - A_1^- &= Y_d/Y_0 (A_d^+ - A_d^-) \end{aligned} \quad (\text{Equation 4.4})$$

Matching the tangential fields at right boundary, we could obtain another two equations:

$$\begin{aligned} LA_d^+ + L^{-1}A_d^- &= A_2^+ + A_2^- \\ Y_d/Y_0 (LA_d^+ - L^{-1}A_d^-) &= A_2^+ - A_2^- \end{aligned} \quad (\text{Equation 4.5})$$

where Y_0 and Y_d are the admittance of the hollow waveguide and the foam-loaded waveguide, respectively.

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After the formulation manipulation, the unknown coefficients were eliminated and the generalized scattering matrix was obtained (Appendix 1):

$$\begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix}$$

when $A_2^- = 0$, the reflection coefficient S_{11} could be simplified as: $S_{11} = A_1^- / A_1^+$, while the transmission coefficient S_{21} could also be simplified as: $S_{21} = A_2^+ / A_1^+$. For any symmetric structures, $S_{11} = S_{22}$ and $S_{21} = S_{12}$.

The general equation of the power for a 2-port network system was as follows. The absorbed power was the power absorbed by the magnetic foam sample.

$$\text{Reflective power} + \text{Transmitted power} + \text{Absorbed power} = 1$$

$$\rightarrow |S_{11}|^2 + |S_{21}|^2 + \text{Absorbed power} = 1 \quad (\text{Equation 4.6})$$

Generally, decibel (dB) format is used to evaluate the intensity or power level of the electromagnetic waves in practical applications.

$$S_{11} \text{ (dB)} = 20 \log |S_{11}| \quad (\text{Equation 4.7})$$

$$S_{21} \text{ (dB)} = 20 \log |S_{21}|$$

The magnitudes of the reflection coefficient S_{11} (dB) and the transmission coefficient S_{21} (dB) in the frequency range of 9 - 11 GHz were obtained from the experimental diagrams directly, as illustrated in Figure 4.47. The magnitude of S_{11} was frequency-dependent but the values were very small, while the magnitude of S_{21} was almost frequency-independent.

Figure 4.47 Experimental diagram of the scattering parameters S_{11} and S_{21} for MF75-55

When the magnitude of S_{11} (dB) was smaller than -15dB, the reflected power $|S_{11}|^2$ could be calculated and would be smaller than 0.032, according to Equation 4.7. This small value could be ignored in the Equation 4.6, i.e. the reflected power was ignored. This applied to all the experimental results of the magnetic foams. Thus, Equation 4.6 could be simplified to

$$|S_{21}|^2 + \text{Absorbed power} = 1 \quad (\text{Equation 4.8})$$

For example, the average magnitude of S_{21} (dB) was 1.28 dB for MF75-55 in Figure 4.47. The absorbed power was 0.255, calculated according to Equation 4.7 and Equation 4.8. This means that 25.5% of the radar power was absorbed by MF75-55.

Figure 4.48 presents the experimental diagrams of the magnitudes of the scattering parameters S_{11} and S_{21} of the low and high density magnetic foams.

Chapter 4 Results and Discussion

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Figure 4.48 Experimental diagrams of the scattering parameters S11 and S21 for the low and high density magnetic foams

As explained in Figure 4.47, by knowing the measured average magnitude of S_{21} , the absorbed power of each magnetic foam was calculated and tabulated in Table 4.12, and plotted in Figure 4.49.

Table 4.12 Calculated absorbed power of the magnetic foams

Sample		Average S_{21} (dB)	$\log S_{21} $	$ S_{21} ^2$	Absorbed power $=1- S_{21} ^2$
Air		-0.0595	-0.002975	0.986	0.014
PU-30		-0.254	-0.0127	0.943	0.057
MFXX-30s	MF25-30	-0.366	-0.0183	0.919	0.081
	MF50-30	-0.591	-0.02955	0.873	0.127
	MF75-30	-0.682	-0.0341	0.855	0.145
MFXX-55s	MF25-55	-0.637	-0.03185	0.863	0.137
	MF50-55	-0.92	-0.046	0.809	0.191
	MF75-55	-1.28	-0.064	0.745	0.255

Figure 4.49 Calculated absorbed power of the magnetic foams

It was found that the absorbed power in air was 1.4%. PU-30 without any carbonyl iron particles was able to absorb 5.7% of the radar power. With the same testing volume, both low and high density magnetic foams showed the same characteristics of the absorbing power, i.e. increasing with the iron content proportionally and significantly. It proved the effective absorbing ability of the carbonyl iron particles in the magnetic foams.

The maximum absorbed power was 25.5% for MF75-55, this was deemed to be insufficient as there are already existing materials that can reach a maximum absorbed power of 99.9% [57].

The radar absorption ability could be enhanced by increasing the density of the magnetic foams or by proper geometric design of the foam, e.g. to be part of a double or multi-layered design, shaping the foam in order to scatter the EM waves besides absorption.

5. Chapter 5 Conclusions

5.1 MF formulation and process development

Low and high density PU foams and five types of magnetic foams (MF25-30, MF50-30, MF75-30, MF25-55 and MF50-55) were successfully synthesized through adequate formulation modifications and/or process modifications.

5.2 MF characterization and properties

The magnetic foams presented open cell structure and good connectivity as observed under stereo-zoom optical microscope, SEM and CT. The carbonyl iron particles were embedded in the polymeric matrix. As the iron content added into the matrix increased, the colour grew darker, the density increased in linear trend, and the particle distribution become worse slightly.

The thermal degradation properties of the PU and magnetic foams were investigated using the thermogravimetric method with nitrogen and air as the furnace atmosphere, respectively. The differential thermogravimetric curves proved that the weight loss rates of the magnetic foams were slower than the pure PU foam. At the early stage of degradation (for example, <10% weight loss), the carbonyl iron particles were found to be able to improve the thermal stability of the magnetic foams in nitrogen, but to deteriorate the thermal stability in air. The effects of heating rate on the thermal degradation were examined. The apparent activation energy of degradation was calculated using the Ozawa's method. The calculated apparent activation energy varied with the degree of conversion or weight loss in both nitrogen and air. At the initial degradation stage, the magnetic foams showed the higher activation energy in nitrogen but the lower activation energy in air. At the later degradation stage, the magnetic foams exhibited the higher activation energy in air.

The mechanical properties under a magnetic field were tested by using 2 fabricated jigs that was capable of producing a magnetic flux density of up to 0.2 Tesla. From the experimental results, it is found that the magnetic foams had a

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slight decrease of compressive strength in the vertical mode of compressive test and a slight increase in the horizontal mode of compressive test. It is concluded that the magnetic foams were not sensitive enough to the magnetic field (0.2 T) applied.

The carbonyl iron contents in the magnetic foams had significant influences to the sound absorbing ability. For both low and high density MFs, the sound absorption coefficient magnitudes were generally higher than the pure PU foams. The developed MFXX-55s could sufficiently absorb more lower frequency sounds, and applied in wider ranges of frequency than the developed MFXX-30s.

The magnetic foams showed effective but not sufficient radar absorbing ability. The absorbed radar power increased with the iron particle content proportionally and significantly.

6. Chapter 6 Recommendations for Future Work

6.1 Synthesis of MFs

The main limitation to load even higher iron particles in the magnetic foams, or to increase the volume fraction of the iron contents during the synthesis, was the density or porosity control of the foams. Although PU-55 and MFX-55s were considered as high density foams, denser foams with smaller cell size and thicker cell walls might increase the possibility for even higher iron particle loading. By increasing the density of MFs, a breakthrough point might occur for the MF to become magnetically sensitive adequately.

6.2 Characterization of MFs

In the radar absorption applications, the complex magnetic permeability (μ_r) and dielectric permittivity (ϵ_r) of the developed MFs, which are two of the most important electromagnetic properties, may be found out by fitting the curves of Figure 4.48.

The scattering parameters S_{11} and S_{21} can be considered as the function of μ_r and ϵ_r , in the format $S_{11}(\mu_r, \epsilon_r)$ and $S_{21}(\mu_r, \epsilon_r)$. An estimated value set of the four real and imaginary components of μ_r and ϵ_r is first provided, then used to calculate the scattering parameters S_{11} and S_{21} . The theoretical results are then compared with the measured data, and this process is repeated to obtain estimated values that produce a set of data that is closest to the measured data.

The sound absorption characteristics of flexible PU foam with carbonyl iron particles incorporated were reported to change when constant intensity magnetic field are applied [58]. An external magnetic field may be applied during the sound absorption tests in future to test the influence of the sound absorption ability of the MFs under the magnetic field.

Properties other than the tested and reported ones in this work may also be carried out to enrich the portfolios of the group of magnetic foams.

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Appendix 1

Figure 4.46 shows how the radar signal interacted with the magnetic foam sample. The parameter l is the length of the foam block. A_1^+ and A_2^- are unknown coefficients of the incident electromagnetic waves from the waveguide port, while A_1^- and A_2^+ are the unknown coefficients of the reflected waves. A_d^+ and A_d^- are the unknown coefficients of the forward and backward electromagnetic waves inside the foam sample.

Figure 0.1 Schematic interaction between the radar signal and the sample magnetic foam

Matching the tangential fields at left boundary, we could obtain the following two equations:

$$A_1^+ + A_1^- = A_d^+ + A_d^- \quad (\text{Equation 1})$$

$$A_1^+ - A_1^- = \frac{Y_d}{Y_0} (A_d^+ - A_d^-) \quad (\text{Equation 2})$$

Matching the tangential fields at right boundary, we could obtain another two equations:

$$LA_d^+ + L^{-1}A_d^- = A_2^+ + A_2^- \quad (\text{Equation 3})$$

$$\frac{Y_d}{Y_0} (LA_d^+ + L^{-1}A_d^-) = A_2^+ - A_2^- \quad (\text{Equation 4})$$

where Y_0 and Y_d are the admittance of the hollow waveguide and the foam-loaded waveguide, respectively.

Appendix 1

if $A_2^- = 0$, Equation 3 becomes:

$$A_2^+ = LA_d^+ + L^{-1}A_d^- \quad (\text{Equation 5})$$

Equation 4 becomes:

$$\frac{Y_d}{Y_0}(LA_d^+ + L^{-1}A_d^-) = A_2^+ = LA_d^+ + L^{-1}A_d^-$$

$$\left[\frac{Y_d}{Y_0} - 1\right]LA_d^+ = \left[\frac{Y_d}{Y_0} + 1\right]L^{-1}A_d^-$$

$$A_d^- = \frac{Y_d - Y_0}{Y_d + Y_0}L^2A_d^+ \quad (\text{Equation 6})$$

Substitute A_d^- into Equation 5,

$$\begin{aligned} A_2^+ &= LA_d^+ + L^{-1}\frac{Y_d - Y_0}{Y_d + Y_0}L^2A_d^+ \\ &= LA_d^+ + \frac{Y_d - Y_0}{Y_d + Y_0}LA_d^+ \\ &= \left(\frac{Y_d - Y_0}{Y_d + Y_0} + 1\right)LA_d^+ \\ &= \frac{2Y_d}{Y_d + Y_0}LA_d^+ \end{aligned} \quad (\text{Equation 7})$$

Equation 1 + Equation 2,

$$2A_1^+ = \left(\frac{Y_d}{Y_0} + 1\right)A_d^+ - \left(\frac{Y_d}{Y_0} - 1\right)A_d^- \quad (\text{Equation 8})$$

Equation 1 – Equation 2,

$$2A_1^- = -\left(\frac{Y_d}{Y_0} - 1\right)A_d^+ + \left(\frac{Y_d}{Y_0} + 1\right)A_d^- \quad (\text{Equation 9})$$

Equation 8/ Equation 9,

$$\text{The reflection coefficient } S_{11} = \frac{A_1^-}{A_1^+}$$

Appendix 1

$$\begin{aligned}
 S_{11} &= \frac{-\left(\frac{Y_d}{Y_0} - 1\right) A_d^+ + \left(\frac{Y_d}{Y_0} + 1\right) A_d^-}{\left(\frac{Y_d}{Y_0} + 1\right) A_d^+ - \left(\frac{Y_d}{Y_0} - 1\right) A_d^-} \\
 &= \frac{-\left(\frac{Y_d}{Y_0} - 1\right) + \left(\frac{Y_d}{Y_0} + 1\right) \frac{A_d^-}{A_d^+}}{\left(\frac{Y_d}{Y_0} + 1\right) - \left(\frac{Y_d}{Y_0} - 1\right) \frac{A_d^-}{A_d^+}}
 \end{aligned}$$

Substitute Equation 6 into the above equation,

$$\begin{aligned}
 S_{11} &= \frac{-\left(\frac{Y_d}{Y_0} - 1\right) + \left(\frac{Y_d}{Y_0} + 1\right) \frac{Y_d - Y_0}{Y_d + Y_0} L^2}{\left(\frac{Y_d}{Y_0} + 1\right) - \left(\frac{Y_d}{Y_0} - 1\right) \frac{Y_d - Y_0}{Y_d + Y_0} L^2} \\
 &= \frac{-(Y_d - Y_0) + (Y_d + Y_0) \frac{Y_d - Y_0}{Y_d + Y_0} L^2}{(Y_d + Y_0) - (Y_d - Y_0) \frac{Y_d - Y_0}{Y_d + Y_0} L^2} \\
 &= \frac{(Y_d + Y_0)[-(Y_d - Y_0) + (Y_d - Y_0) L^2]}{(Y_d + Y_0)^2 - (Y_d - Y_0)^2 L^2} \\
 &= \frac{(Y_d + Y_0)(Y_d - Y_0)(L^2 - 1)}{(Y_d + Y_0)^2 - (Y_d - Y_0)^2 L^2} \\
 &= \frac{(L^2 - 1)}{\frac{Y_d + Y_0}{Y_d - Y_0} - \frac{Y_d - Y_0}{Y_d + Y_0} L^2}
 \end{aligned}$$

The transmission coefficient $S_{21} = \frac{A_2^+}{A_1^+}$

Substitute Equation 6, Equation 7 and Equation 8,

$$S_{21} = \frac{2 \frac{Y_d}{Y_0 + Y_0} L A_d^+}{\left(\frac{Y_d}{Y_0} + 1\right) A_d^+ - \left(\frac{Y_d}{Y_0} - 1\right) A_d^-}$$

$$\begin{aligned}
&= \frac{2 \frac{2Y_d}{Y_d + Y_0} L A_d^+}{\left(\frac{Y_d}{Y_0} + 1\right) A_d^+ - \left(\frac{Y_d}{Y_0} - 1\right) \frac{Y_d - Y_0}{Y_d + Y_0} L^2 A_d^+} \\
&= \frac{\frac{4Y_d Y_0}{Y_d + Y_0} L}{(Y_d + Y_0) - (Y_d - Y_0) \frac{Y_d - Y_0}{Y_d + Y_0} L^2} \\
&= \frac{4Y_d Y_0 L}{(Y_d + Y_0)^2 - (Y_d - Y_0)^2 L^2} \\
&= \frac{4Y_0 Y_d L}{(Y_d + Y_0)^2 - (Y_d - Y_0)^2 L^2}
\end{aligned}$$

Thus, all the unknown coefficients were eliminated in the expressions of S_{11} and S_{21} .