SYNTHESIS AND FRACTURE TOUGHNESS OF MACRO-DEFECT-FREE
(MDF) CEMENT

BY

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THESIS

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Macro-defect-free (MDF) cements were developed following work by the research group led by Birchall at ICI during the late 1970s and early 1980s. MDF cement is a cement-polymer composite seen to provide the high stiffness of a hydrated cementitious material with the high tensile strength of a polymer composite. It is usually made using polyvinyl alcohol (PVA) that undergoes some crosslinking with Al(OH)₆ released as the cement hydrates. It is processed using high shear, typically in a twin roller mill. The most remarkable property of MDF is its high flexural strength, 200-300 MPa as compared to 5–10 MPa for hardened cement pastes. The inventors attributed the high tensile strength to the processing, which they claimed removed large voids otherwise seen in cementitious materials such as Portland cement concrete, hence the basis for the name. Later studies demonstrated that crosslinking occurs between polymer and hydrating cement and that this crosslinking plays an important role in the achievement of high strength. However, there are few reports on the study of the fracture toughness of MDF. A common test, the two-parameter fracture method, based on the simple premise that a change in specimen compliance can be correlated to the length of the effective crack at the time the critical (i.e., peak) load is reached, is used to measure fracture toughness of MDF. With the theory of linear elastic fracture mechanics (LEFM), the loads and displacement associated with crack propagation in notched beams can be analyzed easily. A typical fracture toughness value of 1.6-1.8 MPa · m¹/² was obtained. Also, a microhardness test is used to measure fracture toughness because it suits the form of the specimens and is a simple and expedient experiment, however, it didn’t generate well-identified cracks.
ACKNOWLEDGEMENTS

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Chapter 1

1. INTRODUCTION

1.1 General

Mortar and concrete made using Portland cement, fine/coarse aggregate and water has been a popular construction material thanks to good compressive strength. However, some disadvantages of cement mortar and concrete, such as low tensile strength, low fracture toughness, large drying shrinkage and low chemical resistance, limit their application, particularly for thin section work such as bridge decks [1-3]. However, with the increasing demand being made on cement technology to serve the needs, efforts to overcome these problems have been attempted by incorporating polymer to develop new organic and inorganic cement systems. The addition of small amount of polymer to cement systems started in the 1920’s and many combinations have been studied [1-5]. Some polymer have long-chain structure, which assists in building long-chain network structure of bonding, in contrasting with short-range structure of bonding provided by cement materials [3-4]. Additionally, polymer materials have wide variations in properties, which can provide complex properties to polymer-modified cement/concrete, and therefore present an opportunity to design construction material system with tailored properties. One of the most remarkable polymer-cement composites was developed by Birchall and his coworkers [3-8]. This composite was prepared using calcium aluminate cement (CAC) and polyvinyl alcohol (PVA) with a small amount of water to allow cement hydration. The manufacture of this composite involves high shear mixing, typically in a twin roller mill. The flexural strength of this composite is about 200 MPa, while cement pastes shows values below 15 MPa [4-11]. The inventors attributed the high tensile strength to the processing, which they claimed removed large voids otherwise seen in cementitious materials such as Portland cement concrete, therefore they named this composite macro-defect-free (MDF) cement. However, later studies [15, 16] demonstrated that crosslinking
reaction occurs between polymer and hydrating cement and that this crosslinking plays an important role in the achievement of high strength. Additionally, hot pressing during processing accelerates crosslinking and also causes a dense compaction [15]. Although there is sufficient published literature to discuss the synthesis of MDF and its flexural strength, there are few publications that address the fracture characteristics of MDF. With the principles of linear elastic fracture mechanics, modified two-parameter fracture test was used to quantitatively evaluate the fracture toughness of MDF cement composite.

1.2 Organization of thesis

Investigating mechanical properties of MDF, especially the techniques to measure fracture toughness is the subject of this thesis. The effects of hydrolysis degree of polymer and of ingredients as well as different production parameters on the fracture toughness of MDF cements were also investigated for this purpose. This thesis is divided into the following chapters. Chapter 2 is a literature review discussing the development of MDF, calcium aluminate cement (CAC), polymer (PVA), and the measurement of fracture toughness. Chapter 3 describes experimental procedures, including syntheses MDF cement and testing fracture toughness techniques. Chapter 4 presents the results and discussion of the fracture toughness measurement.
Chapter 2

2. LITERATURE REVIEW

2.1 Macro-defect-free (MDF) composite

Cement based materials have been used extensively in the applications that require compressive strength because the conventional cement pastes are quite weak in tension. In the traditional cast cement-based materials, the water used to provide a sufficient workability of mixture is actually greater than the necessary amount for hydration of cement. When the excess water evaporates, the material becomes more porous which significantly reduce its tensile strength. Therefore, the main drawback of cement based material is its low tensile strength, and low fracture toughness compared to plastics and metals [1-3]. Set cement pastes are as brittle as most ceramics. The hardened cement based material usually contains large defects (flaws or pores) in its microstructure. These defects are largely at the macro level—the large voids in the material caused by air entrapped during mixing, the pores and capillaries formed within the material when water is desiccated during cement hydration, and cracks due to drying shrinkages that occurs during setting and hydration. Cement particles in conventional cast concrete are poorly dispersed and have a tendency to flocculate further; therefore, the packing efficiency of the cement paste is usually low [3-5]. In order to improve fracture toughness and performance under tension of cementitious materials, a large amount of research has been performed to eliminate those large defects from the cement paste by better particle packing in wet and dry states. A number of studies were conducted to decrease the porosity in the cementitious materials and thereby increase the toughness; however, techniques such as polymer impregnation of the pore filling, reducing the w/c ratio in the mixture by adding surfactants, or adding mineral fines as cement paste replacement were not successful to eliminate the formation of macro defects in the material.
At ICI, Birchall and his research group found that introducing a small proportion of water-soluble polymers into the cement and water mix to provide enough plasticity resulted in a reduction of surface tension and inter-particle friction. This allowed particles to pack more closely and significantly decrease usual w/c ratio from 0.5 to 0.11; therefore, the tensile strength and toughness is increased [2-10]. The inventors attributed the high tensile strength to the processing, which they claimed removed large voids otherwise seen in cementitious materials such as Portland cement concrete, hence the basis for the name, macro-defect-free (MDF) cement. MDF was created by using very low w/c ratio (0.08-0.15) with respect to other conventional cementitious materials (0.3-0.7). Cement and soluble-polymer are mixed with water and this mixture is passed through twin roller mill repeatedly until it turns into a dough-like putty. The deformable dough was rolled to eliminate entrapped air bubbles and then molded into the desired shape by extrusion, pressing or other conventional plastic pressing operations. This high shear production process and very low w/c ratio yield the low pore content in this MDF composite. With a hot pressing, the porosity of this composite is further reduced and the high strength is obtained [8-10]. The MDF composite had a flexural strength of 150-200 MPa, a Young’s modulus of 50 GPa, and a compressive strength of 300 MPa [5-11]. Thus, the flexural strength is about 20 times than that of conventional cementitious materials.

2.2 Polyvinyl Alcohol (PVA)

2.2.1 Properties of PVA

Polyvinyl alcohol was first prepared by Hermann and Haehnel in 1924 by hydrolyzing polyvinyl acetate in ethanol with potassium hydroxide [4]. Polyvinyl alcohol is generally produced commercially from polyvinyl acetate by a continuous reaction process. The structure of polyvinyl alcohol (partially hydrolyzed) is shown in Figure 2.1.
The acetate groups are hydrolyzed by ester interchange with methanol in the presence of anhydrous sodium methylate or aqueous sodium hydroxide. However, whether this ester interchange reaction goes to completion depends on the extent of reaction. Thus, PVA is produced by the polymerization of vinyl acetate to poly (vinyl acetate) (PVAc) followed by hydrolysis of PVAc to PVA. The physical characteristics and its specific functional uses depend on the degree of polymerization and the degree of hydrolysis. Current available commercial PVA grades range from high degrees of hydrolysis (above 99%) to low degrees of hydrolysis (below 65%). The overall effect on chemical properties, solubility, and the crystallizability of PVA is generally controlled by the degree of hydrolysis, or the quantity of acetate groups in the polymer. Figure 2.2 shows the solubility of a PVA sample as a function of the degree of hydrolysis at temperatures of 20 and 40 °C. It shows that PVA grades with high degrees of hydrolysis have low solubility in water, and that the high temperatures will increase the solubility of PVA with high degrees of hydrolysis. The presence of acetate groups affects the ability of PVA to crystallize, and PVA grades containing high degrees of hydrolysis are relatively difficult to crystallize [4].
Polyvinyl alcohol is divided into two classes, namely: partially hydrolyzed and fully hydrolyzed. The partially hydrolyzed copolymer is the most widely used polymer for the synthesis of MDF. When the copolymer reacts with water, it will form a ball shape chain because the alcohol groups are hydrophilic and the acetate groups are hydrophobic [5]. Figure 2.3 shows the PVA copolymers reacting with water.

**Figure 2.2: Solubility of a PVA sample as a function of degree of hydrolysis at temperatures of 20 and 40 °C [4]**

**Figure 2.3: PVA copolymer react with water [5]**
2.2.2 Crosslinking of PVA

Polymers are substances that contain a large number of structural units joined by the same type of linkage. These substances often form into a chain-like structure. Chains of polymers join together and produce a three-dimensional network polymer when a material is present which helps to connect parallel chains into a complex molecule. This reaction is called a cross-linking reaction and the material is referred to as a crosslinking agent. Metal ions function as crosslinking agents in some polymers. Crosslinking is a type of bonding that occurs between two chains of polymer. As the amount of crosslinking increases, the polymer become less flexible. Figure 2.4 demonstrates the crosslinking of polymers. The wavy lines between polymer 3 and 4 represent crosslinking bonds.

\[ \text{polymer 1} \] No Cross Linking
\[ \text{polymer 2} \]
\[ \text{polymer 3} \] Cross Linked
\[ \text{polymer 4} \]

\[ \square = \text{monomer} \]

\textit{Figure 2.4: Crosslinking of copolymers [5]}

2.3 Calcium Aluminate Cement (CAC)

Calcium aluminate cement (CAC) is a unique class of cement that is different from ordinary Portland cement (OPC), particularly due to the chemical make-up. CAC contains a far greater amount of alumina and a far less amount of silica. Table 2.1 shows the major chemical compositions of CAC and OPC.
Generally, CAC has a significantly higher early strength gain (upwards of 41 Mpa at 6 hours of age at 20 °C) and a higher heat of hydration than OPC. The high early heat and strength gain makes CAC attractive, especially during the winter months and/or when rapid repairs are needed [17-19].

2.4 CAC-PVA interaction

The polymer used in the synthesis of MDF cements was initially considered only as a rheological aid and a filling agent to facilitate particle packing as well as reduce the material porosity [2-8]. The inventors claimed that the high strength of MDF cement composite is due to the elimination of larger critical flaws which normally reduce the strength of conventional cast cement pastes. However, later studies by Popoola et al. and Rodger et al. [3-7] on the chemistry and the microstructure of the calcium aluminate MDF materials have attributed the significant improvements of the mechanical properties of these materials to the chemical reactions occurring between the PVA polymer (the polyvinyl alcohol) arising from the PVAc hydrolysis) and the inorganic ions produced when the cement dissolves in water. When cement and partially hydrolyzed PVA reacts with water, hydrolysis of the acetate groups will take place as the pH rises. It has been suggested that (Al(OH)4) ions released by the calcium aluminate cement cross-link the polyvinyl alcohol chain in the way structured [5-7]. The polymer phase crosslinks with Al in

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ordinary Portland Cement (%)</th>
<th>Calcium Aluminate Cement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3S</td>
<td>50-70</td>
<td>0</td>
</tr>
<tr>
<td>C2S</td>
<td>15-30</td>
<td>&lt;10</td>
</tr>
<tr>
<td>C3A</td>
<td>5-10</td>
<td>0</td>
</tr>
<tr>
<td>C4AF</td>
<td>5-15</td>
<td>10-40</td>
</tr>
<tr>
<td>CA</td>
<td>0</td>
<td>40-50</td>
</tr>
</tbody>
</table>
calcium aluminate cement, and the polymer acts as a continuous matrix phase. Therefore, the mixture became rubbery and allowed the physical processing of polymer cement mix.

Later studies [8-15] on the fracture behavior of polymer modified cements showed that the reduction or elimination of the macro pores alone could not result in significantly improved mechanical properties of the composite [13-15]. They used a latex-type polymer-modified cement composite that had much smaller or fewer macro pores than the PVA/CAC MDF system. The bonding between latex type polymers and the inorganic phase was not as strong as the PVA/CAC MDF system. Therefore, the latex modified cement had a much lower strength than PVA/CAC MDF cement. Their studies confirmed the hypothesis that the polymer contributed more to the MDF composite than just being a rheological aid for processing.

2.5 Fracture mechanics

The main difficulty in designing high strength materials is the presence of defects (such as cracks and voids) that can concentrate the local stresses to such an extent that a crack exceeds its critical length, and propagates dramatically through the material to lead to structural failure. Griffith [4-6] in 1921 found that there were many microscopic cracks which were present at all times in every material. He believes that these small cracks actually lowered the ultimate strength of the material, because as the load is applied to these cracks, stress concentration occurs. Griffith proposed the energy-balance concept of fracture based on the principle of energy conservation laws of mechanics and thermodynamics [4-6]. Griffith’s theory provided a fundamental starting point for fracture mechanics in which the operative forces could be considered conservative. For some materials like concrete, rock, and soda glass, sudden failure was observed; while for some materials like metals, it was discovered that large deformations at a constant stress were needed. Therefore, the fracture toughness indicates the relationships between the crack length, the inherent ability of material to resist crack growth, and the stress at which a critical crack length causes failure [4-10]. Fracture toughness reflects the capability of the material to resist failure in the presence of cracks [5]. After
Griffith introduced the theory of fracture mechanics, Irwin [7-8] in the 1950s continued to study Griffin’s theory on ductile materials. He found that a certain energy from plastic deformation should be considered in addition to the strain energy originally proposed by Griffith. In Irwin’s linear elastic fracture mechanics model, he assumes materials have a small scale yielding, which is where the size of the plastic zone is much smaller compared to the crack length. However, this assumption is limited for certain types of materials (such as steels).

For most engineering materials, linear elastic fracture mechanics may not be valid all the time. Such materials show some non-linear elastic and inelastic behavior under applied loads. Therefore, they are several modes to measure the fracture toughness of materials showing elastic-plastic behavior. Irwin’s R-curve model is an early attempt. He developed the crack growth resistance curve (R-curve), which is based on the relationship between the resistances to fracture and growing crack size in elastic-plastic materials [6-7]. The R-curve reflects the total energy dissipation rate as a function of the crack size, and it can be used for materials showing unstable crack growth and slow stable fracture [6-9]. Wells et al. [7-15] using a crack opening displacement under load model to conclude that fracture usually occurs when the crack tip opening (CTOD) reaches a critical value. Wells believes that the CTOD fracture model is appealing because this criterion is independent of whether linear elastic fracture mechanics (LFEM) applies or not [8-10]. He successfully developed a fracture test that initiated in pre-cracked specimens at low stress to model fracture under conditions of large plastic deformation [9-10].

2.6 Fracture toughness $K_{IC}$

A parameter—the stress intensity factor (K)—is normally used to determine the fracture toughness of materials. The fracture toughness, $K_{IC}$ (units: MPa\*m$^{1/2}$) measures the resistance of a material to the propagation of a crack. The Roman numeral subscript represents the mode of fracture. There are three fracture modes (shown in Figure 2.5): mode I is an opening or tensile mode, mode II is a sliding or in-plane shear mode, and mode III is a tearing or antiplane shear mode.
There are two general methods to measure fracture toughness in engineering materials. One is to measure the critical stress intensity (K_{IC}) in plane strain by measuring stress required to propagate a sharp crack, and the other is to measure the energy absorbed in a rapid fracture of a bar (Charpy test) [10-12]. The Charpy test uses a square bar with a small notch, and it measures the absorption of energy by the pendulum impact. It is a macroscopic level test but it has a crack nucleation process [11]. Therefore, higher toughness results in higher energy absorbed. Measuring critical stress intensity factor (K_{IC}) is a quantity method corresponding to the loading, crack size, and structural geometry.

2.7 Two parameter fracture model

Jenq & Shah have proposed two parameter fracture model. The two parameters are critical stress intensity factor calculated at the tip of the effective crack and critical crack mouth opening [11-13]. As the specimen is loaded, the compliance of the pre-peak load versus crack mouth opening displacement (initial compliance, C_I) is measured. Using this initial compliance, C_I, and the initial crack length, a_0, the elastic modulus, E, of the concrete can be determined. After the specimen reaches the peak load, it is unloaded (at 95% of the peak load) and the compliance of the unloading response, C_u, is determined. The critical effective crack length, a_e, is determined using an iterative based on the unloading compliance, C_u, and the elastic modulus, E. The fracture toughness, K_{IC},
and the critical crack tip opening displacement, CTOD\(_C\), are determined from the critical effective crack length, \(a_e\), and the peak load, \(\text{Load}_C\) [12].

2.8 Indentation fracture toughness

Compared with inorganic glasses and ceramics, indentation fracture mechanics researches have been rarely reported for polymer-cement materials, in spite of the advantages of low-cost and directly determination of fracture toughness using only small amounts of materials [5-11]. The concept of measuring cracks created by hardness indentations originated with Palmqvist in the 1950s [5-7]. Because this technique can determine the fracture toughness rapidly, it achieved popularity very quickly. Although it is a rather non-conventional approach for determining the fracture toughness \(K_{IC}\), it seems to be a convenient way to perform the experiment. It requires only a small volume of material and the actual measurements can be quickly completed with only a short sample preparation time and at a minimum financial cost [6-10]. Fracture toughness determination by the indentation technique generally required a smoothly polished test specimen surface, and the specimen is not precracked. Then, the polished specimen surface is indented by a Vickers pyramidal microhardness indenter. It can be done by a conventional hardness testing machine. The load will be gradually applied to the indenter to peak load, and the load will be hold for a set dwell period and then unload the indenter. The sample is indented at a high testing load to create a deformed region beneath and in the vicinity of the impression, which leads to the generation of four cracks emanating from the corners of the square Vickers diamond impression [6-11]. The lengths of the cracks, along with the indentation load, the impression size, the hardness and elastic modulus of the material, and an empirical calibration constant are used to compute the fracture toughness of the material [5-11]. Equation 1 shows the relationship between measured crack lengths and the fracture toughness of a material [10-11].

\[
K_c = \chi \left( \frac{E}{H} \right)^{1/2} \frac{P}{a^{3/2}}
\]

(1)
where $P$ is the applied load, $E$ is Young’s modulus, $H$ is the Vickers hardness, $a$ is the radial crack length measured from the center of the indent, and $\chi$ is an empirically determined “calibration” constant.
Chapter 3

3. EXPERIMENTAL PROCEDURE

Macro-defect-free (MDF) cements are polymer-cement composites consisting of a chemically bound 3-D network of cement grains embedded in a polymer matrix. The typical standard processing method starts with pre-mixed dry raw materials made up of calcium aluminate cement (CAC), and partially hydrolyzed polyvinyl alcohol (PVA), and finishes with the addition of water and a small amount of glycerol to form a damp, granular and cohesive mix. Then the mix undergoes a shear mixing on a twin roller mill to form a sheet. The last step in production of a MDF sheet is hot press and curing at 80 °C. Although the twin roller mill has been used successfully for making high flexural strength MDF sheets [4], the production procedure should be tightly controlled. Factors, such as temperature, humidity, mixing time and speed of the mills (shear rate), will significantly affect the quality of MDF sheets. Without an adequate control of these factors, inconsistent mechanical properties of MDF sheets were found. In order to understand the science behind the mechanical properties of MDF, especially fracture toughness, PVAc with different particle size distribution and degree of hydrolysis were used.

3.1 Materials

The polymer used in this study was partially hydrolyzed polyvinyl alcohol (PVA). It is produced by Sekisui Chemical Co. with different degree of hydrolysis: 87%, 88%, 93% and 98.8%, and Sigma-Aldrich Co. with degree of hydrolysis 80%. The main properties of PVAs used for this study are summarized in Table 3.1. The cement used in this study was calcium aluminate cement which was produced by Kerneos Inc., with the commercial name of Ternal W. Ternal W is the newest grade of white calcium aluminate cement for the construction industry. It has essentially the same composition as Secar 71 which is commonly used for synthesizing MDF. Ternal W cement has an
Al₂O₃ content of 70% and a CaO content of 29%. The detailed technical properties of Ternal W are listed in Table 3.2.

Table 3.1: Properties of hydrolyzed poly (vinyl alcohol-acetate) copolymer (PVA) [11]

<table>
<thead>
<tr>
<th>PVA grade</th>
<th>Viscosity (cP)</th>
<th>Particle Size Grade</th>
<th>% Hydrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>SELVOL 107</td>
<td>5.5-6.5</td>
<td>Fine</td>
<td>98.8%</td>
</tr>
<tr>
<td>SELVOL 418</td>
<td>14.5-19.5</td>
<td>Fine</td>
<td>93%</td>
</tr>
<tr>
<td>SELVOL 513</td>
<td>13.0-15.0</td>
<td>Fine</td>
<td>88%</td>
</tr>
<tr>
<td>SELVOL 205 S</td>
<td>5.2-6.2</td>
<td>Ultra-Fine</td>
<td>87%</td>
</tr>
<tr>
<td>Sigma-Aldrich 360627</td>
<td>__</td>
<td>Coarse</td>
<td>80%</td>
</tr>
</tbody>
</table>

Table 3.2: Chemical composition of calcium aluminate cement Ternal W [12]

<table>
<thead>
<tr>
<th>Main constituents</th>
<th>Usual range</th>
<th>Specification limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ (%)</td>
<td>68.7 - 70.5</td>
<td>&gt; 68.5</td>
</tr>
<tr>
<td>CaO (%)</td>
<td>28.5 - 30.5</td>
<td>&lt; 31</td>
</tr>
<tr>
<td>SiO₂ (%)</td>
<td>0.2 - 0.6</td>
<td>&lt; 0.8</td>
</tr>
<tr>
<td>Fe₂O₃ (%)</td>
<td>0.1 - 0.2</td>
<td>&lt; 0.4</td>
</tr>
<tr>
<td>MgO (%)</td>
<td>&lt; 0.5</td>
<td></td>
</tr>
<tr>
<td>TiO₂ (%)</td>
<td>&lt; 0.4</td>
<td></td>
</tr>
<tr>
<td>K₂O+Na₂O (%)</td>
<td>&lt; 0.5</td>
<td></td>
</tr>
</tbody>
</table>

3.2 Material Composition

The basic composition of the MDF composite was proposed according to literature [1-12] and to previous experimental experiences (shown in Table 3.3). Composition and volume of the
components forming MDF composite were considered as the main influence on properties of the material. The material composition for making MDF was modified based on the literature and previous experimental experiences to get the optimized w/c ratio and polymer/cement ratio. This is because the optimum w/c ratio is different for each calcium aluminate cement and each polymer. According to the literature [5-12], the best PVA used for making MDF is Gohsenol KH17. However, due the Gohsenol KH17 is not available, the optimized w/c ratio and PVA/cement ratio cannot transfer to the new PVA used. The particle size distribution of PVA can be important for determining both the optimum w/c ratio and polymer/cement ratio. Therefore, optimization of the material composition was done at the beginning of this study.

Table 3.3: Typical material composition for making MDF

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
<th>Weight (g)</th>
<th>Weight (%)</th>
<th>Volume (cm³)</th>
<th>Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAC</td>
<td>2.93</td>
<td>120</td>
<td>84.2</td>
<td>40.96</td>
<td>67</td>
</tr>
<tr>
<td>PVA</td>
<td>1.30</td>
<td>8.4</td>
<td>5.9</td>
<td>6.46</td>
<td>10</td>
</tr>
<tr>
<td>Glycerol</td>
<td>1.26</td>
<td>0.84</td>
<td>0.6</td>
<td>0.67</td>
<td>1</td>
</tr>
<tr>
<td>Water</td>
<td>1</td>
<td>13.2</td>
<td>9.3</td>
<td>13.20</td>
<td>22</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>142.44</td>
<td>100</td>
<td>61.28</td>
<td>100</td>
</tr>
</tbody>
</table>

3.3 Procedure

The procedure of producing the MDF composite mainly consisted of mixing, high shear processing, and hot pressing steps. The mechanical properties of MDF cement are very sensitive to any flaws generated in the production process. Therefore, each step had to be carefully controlled to avoid introducing flaws in production. The following procedures were used to make MDF sheets.

3.3.1 Preparation
The platens of the hot press were preheated to 80°C (176 °F) and the water cooling system for the twin roller mill was set to 15°C (60 °F) before production of MDF to ensure the temperature was well controlled for high shear processing and hot press. The nip gap was set to 0.25 mm and the side guards were set to be 14 cm. (5.5 inches) apart before running the twin roller mill. The initial roller speed was set to 36:30 (front: back). The preparation steps minimized the MDF production time to avoid drying of mixed raw materials and to prevent formed MDF sheets from crumbling before hot pressing.

3.3.2 Mixing

The mixing of components is another important part of the MDF production. The components were mixed together to achieve a mix as homogeneous as possible. Greater degree of mixing is presumed to enhance polymer cross linking during cement hydration. Firstly, the CAC and PVA were properly premixed in a conventional 5-speed Kitchen Aid mixer in speed 1 for two minutes before adding the water and glycerol. The solution was prepared from exact volume of distilled water and glycerol. Secondly, after adding of glycerol and water, the batch was mixed for one minute at medium speed (speed rate 3) to form a damp, granular and cohesive mix formed. Thirdly, a knife was used to scrape off the materials sticking in the bowl in 30 seconds and mixed them in another one and half minute at speed rate 3. This mixing sequence was essential to achieve intimate contact between the polymer, water and cement. Figure 3.1 shows the mixing of all components in Kitchen Aid mixer.
3.3.3 High shear processing

The MDF composite production used a twin roller mill (model 400, 6x15 inch (15.2x38.1 cm) laboratory mill, Stanat Mfg, Long Island, NY in Figure 3.2) to provide high shear processing. The twin roller mill allows a satisfactory homogenous mix to form in less than 5 minutes because it can provide very high shear rate.
The processing time on twin roller mill to some extent depends on how rubbery of MDF sheets (typical in 10 minutes). In general, longer processing time was require to high w/c ratio MDF sheet to reach sufficient stiffness and plasticity. Twin rollers mill were moved to adjust the nip gap between the rolls. The rolls rotated counter to each other, and the speed of each roll was controlled manually. The mix was fed into the nip gap of the twin roller mill, and the nip gap and the speed rate were adjusted for each passing.

Between each pass, a paper towel was used to clean the knife blade to ensure no residue material was left on it. If necessary, the surface of the twin roller mill was also needs to be wiped clean to avoid formation of induced defects in the following passing. After several times of passing through, the formed MDF sheet could be peeled off from the rollers or dropped off by itself. The sheet was caught by hand if it dropped off by itself so it does not fall onto the table base below the twin roller mill where the residue debris collect. It was found that cracking formed in some MDF samples after the samples were undergone hot pressing. The cracking was attributed to the combining of high w/c ratio and long shear mixing. Therefore, the time of shear mixing on twin roller mill was adjusted according to the w/c ratio used for MDF production. No further mechanical tests were performed on those cracked samples.

3.3.4 Hot press and curing

For the single layer MDF samples

After the MDF sheet was removed from the twin roller mill, it was trimmed with a razor blade. Then, the MDF sheet was put between two sheets of 0.15 mm thick, clear Mylar® polyester plastic for hot pressing and curing. The purpose of Mylar® plastic sheets is to provide a non-stick surface and to produce a smooth finish on MDF samples. All the MDF sheets were pressed at 80°C and 5 MPa for 10 minutes between two aluminum plates (shown in Figure 3.3) in hot press (Model 2518, Carver Press Co., Menomonee Falls, WI). All the specimens were then cured in an oven at 80°C
for 24 hours between 2 sheets of Mylar® and aluminum plates. The purpose of covering the specimens with Mylar® and adding aluminum plates on top as weight was to avoid curling of the specimens. After 24 hours curing, the samples were taken out of the oven and stored in a desiccator.

For the multi-layer MDF samples

Multi-layer MDF samples were made by trimming the MDF sheets into 2” x 5”pieces and five sheets were stacked. In order to get well-bonded multi-layer sample, the sample was passed through the twin roller mill again to eliminate flaws and laminations between layers. The nip gap of twin roll mill was widened to fit the thickness of multi-layer MDF sample. Then, those multi-layer MDF sheet was placed between two sheets of 0.15 mm thick, clear Mylar® polyester plastic to undergo hot press followed the same procedures as the single layer MDF samples. Figure 3.4 shows the multi-layer MDF sample after hot press and curing.

![Figure 3.3: Hot press machine](image-url)
For the MDF beam samples

The MDF beam samples were made by trimming the MDF sheets into 1" x 6" pieces (Figure 3.5 and 3.6). After stacking seven multiple MDF sheets together, the sample was put into a 1" x 1" x 6" steel mold in Figure 3.7. The steel mold with top cover was pressed at 80°C and 15 MPa for 15 minutes. The beam MDF sample was demolded after hot pressing and cured in an oven at 80°C for 24 hours between 2 sheets of Mylar® and aluminum plates.
**Figure 3.5**: MDF sheets sample before trimming

**Figure 3.6**: MDF sheets sample after trimming
3.3.5 Notched samples for fracture toughness

The notches in multi-layer and beam MDF samples were cut by IsoMet® Low Speed Saw (Figure 3.8). The sample was fixed by holding arm, which incorporates a precise micrometer adjustment for alignment of specimen prior to sectioning. Using low speeds (0-300 rpm) coupled with diamond watering blades, this saw provides a notch can achieve an "as-cut" surface which is generally free of damage. The ratio of the span to the depth of the beam (S/D) was 5.5 for all the specimens. The ratio of the notch length to the beam depth (a₀/D) was 0.25 for all the specimens. The thickness of all beams was equal to the beam depth. To measure crack mouth opening displacement (CMOD) a pair of knife edges is attached at the two sides of a performed notch on the lower surface of the beam.
3.4 Methods of Testing

3.4.1 Biaxial Flexural Strength Test

Specimens for biaxial flexural strength testing were prepared by pressing a circular steel cutter with 2.54 cm diameter into the MDF sheet finished from twin roller mills. For each batch, a minimum of five disc-shaped specimens were prepared, and then all specimens were hot pressed and cured. After curing, they were stored in a desiccator at ambient temperature until testing.

The flexural strength of the composite material was tested following the method developed by Wachtman et al. [15], originally developed for ceramic substrates. ASTM F394-78 (1996) was published according to Wachtman’s proposals.

A test disc-shape sample with a nominal diameter of 1 inch was supported symmetrically on three ball bearings near the periphery of disc and equidistant from its center. The load is applied at the center of the disc sample with a 1.588-mm diameter piston. The equipment used in performing the test is an Instron Model 5500R load frame. The load rate was controlled by the speed of the
crosshead, which has a 100-kN load cell attached. The loading program is under crosshead control and the crosshead speed was 0.15 mm/min to avoid dynamic punch failure of the specimen. With the load at failure sensed by the load cell, the flexural strength of the specimen was calculated. The loading fixture is showing in Figure 3.8.

![Loading fixture of biaxial flexural strength testing](image)

**Figure 3.9: Loading fixture of biaxial flexural strength testing**

The formula for calculating flexural strength of MDF is [15]:

\[ S = -0.2387P(X - Y) d^2 \]

where;

\[ X = (1+\nu)\ln(B/C)^2 + \frac{(1-\nu)}{2}(B/C)^2 \]
\[ Y = (1+\nu)\left[1+\ln(A/C)^2\right]+(1-\nu)(A/C)^2 \]

S: Biaxial Flexural Strength or MOR, MPa.
P: Failure Load, N.

\( \nu \): Poisson Ratio.

d: Thickness of the specimen, mm.

A: Radius of support circle, mm.

B: Radius of loaded area or ram tip, mm.

C: Radius of specimen, mm.

It should be noted that Poisson ratio was accepted as 0.26 for all specimens, which was adapted from test method of MDF cement in research literatures. Five specimens were prepared and tested for a representative flexural strength of each material.

### 3.4.2 Indentation fracture testing

Indentation techniques for assessing fracture toughness are attractive due to the simplicity and expediency of experiments. Sample preparation is usually necessary with a microhardness test in order to provide a small enough specimen that can fit into the tester [18-22]. Additionally, the sample preparation will need to make the specimen’s surface smooth to permit a regular indentation shape and good measurement, and to ensure the sample can be held perpendicular to the indenter. Before cutting, the sample was polished by using METPOL series of grinding/polishing machines with 600 grit sandpaper at speed of 100 rpm. Mineral oil was used to lubricate since MDF material is water sensitivity. After the sample was polished, IsoMet® Low Speed Saw was used to cut the sample into 1 cm x 1 cm square. The prepared samples were mounted in a plastic medium to facilitate the preparation and testing. The microhardness tester used for testing is Leitz Wetzlar Microhardness Tester (Figure 3.9). The equipment has Microloads of 5, 10, 15, 25, 50, 100, 200, 300 and 500 gms in addition to basic load of 5±0.005 gms and is equipped with 10x and 50x objectives. The 50x has graduated scale with the help of which the scale indentation diagonals can be measured.
3.4.3 Fracture toughness testing

Two-parameter fracture model developed by Shah and Jenq [17] was adopted for fracture toughness testing on MDF samples. This two parameter fracture model is proposed to include nonlinear slow crack growth. Critical stress intensity factor, $K_{IC}$, is calculated at the tip of the effective crack. The critical effective crack extension is dictated by the elastic critical crack tip opening displacement, $CTOD_c$. Two-parameter fracture model was performed in a closed-loop testing machine with displacement as the feedback signal to generate a stable failure during the loading.

The three point bending test was performed by an Instron 5500R load frame with a 100-kN load cell. The applied load was controlled by a constant rate of increment of crack mouth opening displacement (CMOD) measured using a CMOD gauge, which was positioned on the bottom of the specimens using knife edges. With the displacement control, cycles of loading and unloading are applied. On each loading cycle, unloading is at about 95% of the peak load reached. The details
of properties calculated from the load-CMOD curve can be found in Appendix. Figure 3.9 shows the three point bending on notched MDF beam.

![Figure 3.11: Three point bending on notched MDF beam](image)
Chapter 4

4. RESULTS AND DISCUSSIONS

4.1 Synthesis of macro-defect-free (MDF) cement

MDF cements were successfully produced by using the procedures mentioned in the previous chapter. Production was successful with four of these polymers, but MDF cements could not be produced with only fully hydrolyzed PVAc (hydrolysis degree 99.3%) even with modified producing procedure. It is found that the water/cement ratio is critical for making successful MDF cements. If the water/cement ratio is too high, the mixture will be too sticky to work with on the twin rollers mill (shown in Figure 4.1). If the water/cement ratio is too low, the mixture will be crumble and stiff that cannot form MDF sheet on the twin rollers mill (shown in Figure 4.2). Figure 4.3 shows an ideal water/cement ratio MDF mixture before high shear processing.

![Figure 4.1: MDF cement mixture with high w/c ratio](image_url)
Resultant product produced with fully hydrolyzed PVAc can be seen in Figure 4.4. All trails were unsuccessful with fully hydrolyzed PVAc even with the modified procedure in different w/c and p/c ratios. It is very hard to pass through the mixture between twin rollers mill, and the mixtures
become hot to touch. The formed dough tended to debond from the faster roll and even the formed MDF sheet a tendency to delaminate.

![Unsuccessful MDF cement with fully hydrolyzed PVAc](image)

*Figure 4.4: Unsuccessful MDF cement with fully hydrolyzed PVAc*

Table 4.1 shows the optimized water/cement ratio (w/c ratio) and polymer/cement ratio (p/c ratio) to make successful MDF cements. It is really difficult to peel off the sheet from rolling mills if your w/c ratio is 0.18. The turning cycle of the sheet needs to be increased if you would like to peel off MDF more easily at that w/c ratio, but it is not also practical. The reason is that it may take extra time to easily peel off the MDF sheet (Maybe takes 30 minutes depends on the properties of cement and PVA used). Therefore, the optimized of w/c and p/c ratio is to get the best consistency of dough so that the MDF sheet formed on the twin rollers mill can be peeled off easily with hands.

*Table 4.1: Optimized w/c, p/c ratio for MDF cements*

<table>
<thead>
<tr>
<th>Polymer</th>
<th>% Hydrolysis</th>
<th>Best w/c ratio</th>
<th>P/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fully hydrolyzed</td>
<td>98%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Intermediate hydrolyzed</td>
<td>91-93%</td>
<td>0.16</td>
<td>0.07</td>
</tr>
<tr>
<td>Partially hydrolyzed</td>
<td>80%</td>
<td>0.14</td>
<td>0.07</td>
</tr>
<tr>
<td>Fine partially hydrolyzed</td>
<td>87-89%</td>
<td>0.15</td>
<td>0.08</td>
</tr>
</tbody>
</table>
In order to get a better control in making MDF cements and to get a consistency replicate samples for later biaxial flexural strength and fracture toughness testing, the optimized setting of twin rollers mill was also used after several trails. Table 4.2 shows the optimized setting for the twin rollers mill. All the MDF cements samples prepared were followed the same setting in Table 4.2.

Table 4.2: The setting of twin rollers mill for every pass

<table>
<thead>
<tr>
<th>Side Guards (mm)</th>
<th>Nip Gap (mm)</th>
<th>Speed rate (Front : back)</th>
<th>Operations</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>0.25</td>
<td>37:30</td>
<td>Each mixing was passed three times and folded after each pass. Material was stripped in each pass with the knife blade equipped on twin roller mill until dough was cohesive.</td>
</tr>
<tr>
<td>140</td>
<td>0.49</td>
<td>37:30</td>
<td>The nip gap was increased for two turns (to 0.49 mm) and folding, passing through again.</td>
</tr>
<tr>
<td>140</td>
<td>0.49</td>
<td>58:29</td>
<td>Shear mixing for 15 seconds and rotating the sample 90 degree to shear mixing for another 15 seconds. The formed sheet adhered to the front roll in this process.</td>
</tr>
<tr>
<td>140</td>
<td>1.66</td>
<td>37:30</td>
<td>The nip gap was increased to 1.66 mm and fold sheet triple. Passing through with rotating 90 degree each time.</td>
</tr>
<tr>
<td>Removed</td>
<td>1.66</td>
<td>30:30</td>
<td>Eight passes with sheet folded and rotated 90 degree between passes to get a continuous sheet.</td>
</tr>
<tr>
<td>Removed</td>
<td>-</td>
<td>30:30</td>
<td>Only for double or multiple layers of MDF.</td>
</tr>
</tbody>
</table>

4.2 Biaxial Flexural Strength

4.2.1 Effects of particle size of PVA
Since the PVA samples used in this study have different particle size in their manufacture specification. The flexural strength of MDF material with different particle size was measured. Figure 4.5 shows the biaxial flexural strength results of MDF cement samples with different PVA particle size (same hydrolysis degree 80% in PVA). It can be found that PVA particle size significantly affect the flexural strength of MDF. The average flexural strength decreases significantly from 201 MPa to 51 MPa when the coarse PVA (36 μm) was used for making MDF samples. The ultra-fine PVA (6 μm) yields the highest flexural strength 201 MPa. This implies an increase of 74% in flexural strength with ultra-fine PVA particle used for production. The scattering of the flexural strength data in Figure 4.5 was attributed to processing induced flaws were not completely avoided.

![Figure 4.5: Biaxial flexural strength with different PVA particle size](image)

PVA in large particles may not dissolve completely in water, and it does not form bulk phase in MDF. The degree of crosslink could be much lower, resulting low flexural strength. An optical microscope image shows undissolved polymer phase in MDF cements in Figure 4.6
4.2.2 Effects of polymer content on MDF cements

Effect of polymer content can be seen in Figure 4.7. If we compare with 7\% polymer content (PVAc/cement=0.07) and 5\% polymer content (PVAc/cement: 0.05), there is about 56 \% increase in PVA with ultra-fine grade and fine grade. However, with increased polymer content to 9\% in MDF cement, it does not increase the flexural strength. There is about 17\% decrease in flexural strength in both ultra-fine grade and fine grade polymer. Using 7 \% PVAc/cement ratio gives highest flexural strength, therefore 7 \% PVAc/cement ratio was accepted for further productions in fracture toughness testing.
4.3 Indentation fracture toughness

The indentation-strength technique was found not effective to MDF cements for measuring fracture toughness. The main problem using this technique is no well-developed cracks at the indent corners. During Vickers indentation, with increasing indentation loads, there is a transition during the development of the cracks about the impression. For low test loads, the indentation begins as a crack-free pyramidal microhardness impression. It then evolves or transforms to an impression with individual cracks emanating from the four corners of the impression at the surface, but also containing an extensive crack pattern beneath the surface. However, it experiences extensive lateral cracking and often considerable spalling about the impression for the higher indentation test loads and longer dwell period as shown in Figure 4.9, and 4.10. All the figures were cracks decorated. Figure 4.8 shows three identified individual cracks emanating from the corners of the impression at the surface. Figure 4.9 shows the lateral cracking on the side of the impression, and Figure 4.10 shows spalling occurred at lower corner of the impression.
Figure 4.8: Identified individual cracks emanating from the corners of the impression

Figure 4.9: Identified lateral cracking on the side of the impression
Figure 4.10: Identified spalling occurred at lower corner of the impression

The possible reasons for unsuccessful indentation fracture testing are the load may not high enough to initiate the cracks at the corners of impression due to the maximum load equipped with the microhardness tester; the MDF cements materials might too ductile to produce any fractures due to the polymers in MDF. There is no literatures addressed using indentation to determine toughness of polymers simply probably due to the cracks cannot be initiated. Thus, the indentation-strength technique was not effective to MDF cements for measuring fracture toughness.

4.4 Two parameter fracture model in MDF

The typical load versus crack mouth opening displacement (CMOD) for tested MDF beam specimens can be seen in Figure 4.11. From the load-CMOD curve, it can be seen that the initial part of the curve is nearly linear and the CMOD of the tip of the notch which is tension strain can be increased with load growing. After a linear portion of the load-CMOD curve, the load reaches the peak quickly.
Figure 4.11: Load versus crack mouth opening displacement (CMOD) for tested MDF specimens

From the load-CMOD curves in Figure 4.11, the MDF cements behave as an elastic-brittle material since the rapid decrease in strength immediately after peak load. This brittle behavior is commonly found in high strength concrete, and it makes difficult to initiate unloading at exactly 95% of the peak load. Figure 4.12 shows load versus CMOD for tested cement paste specimen. After specimen reached peak (cracked), the load of cement paste is lower than that of MDF for the same CMOD.
From these phenomena, one can see that MDF have better fracture properties than cement paste. The fracture toughness $K_{IC}$ of MDF specimen in Figure 4.11 is about $1.79 \text{ MPa} \cdot \text{m}^{1/2}$ and the Young’s modulus $E$ is about $42.8 \text{ GPa}$.

![Figure 4.12: Load versus crack mouth opening displacement (CMOD) for tested cement paste](image)

4.4.1 Effects of polymer content on fracture toughness of MDF cements

The effects of different polymer content in MDF cements on fracture toughness was studied. Figure 4.13 shows the fracture toughness of MDF with different polymer content (constant w/c ratio). It can be found that MDF with 7% polymer content has the highest fracture toughness in this study. Polymer content higher or lower than 7% will both decrease the fracture toughness of MDF. The changes of polymer content is considered a change to the degree of crosslink and a change in the polymer bulk phase content in MDF material. However, it was not easy to produce MDF cement
with 4% PVA content and MDF sheets passed from roller mills several times more, because it is hard to peel of the sheet from rollers mill. Higher shear processing was required for drying.

Optical microscope was used to examine the fracture surface of MDF cements after the testing. It was found that the MDF cements with low polymer content showed some microcracks at the fracture surface, while the MDF cements with high polymer content showed less microcracks in fracture surface. It suspect that microcracking could be the toughening mechanism for low-polymer MDF cements. Future research is needed to identify the onset of microcracking prior to loading.

![Figure 4.13: Fracture toughness of MDF with different polymer content](image)

**Figure 4.13: Fracture toughness of MDF with different polymer content**

4.4.2 Effects of high shear processing direction on fracture toughness of MDF cements

MDF cements were folded 2 or 3 times at the last step of calendaring, and the samples were rotated 90 degree to shear processing. These tests were conducted in order to see the effects of shear processing direction on the fracture toughness of MDF cements. Two extra cases were studied beside the optimized shear processing setting (samples were rotated—mix direction). The MDF
sheets were not rotated during the shear processing, so only one processing direction was applied on twin rollers mill. One case is the loading direction is parallel to the shear processing direction on twin rollers mill (parallel); and the other case is the loading direction is perpendicular to the shear processing direction on twin rollers mill (perpendicular). Test results can be seen in Figure 4.14. The mix direction is the control group, which was used for producing MDF cements sample. It can be seen that the shear processing direction has an impact on the fracture toughness of MDF cements. When the loading direction is parallel to its shear processing direction, the MDF cements has the lowest fracture toughness among these three cases. The possible explanation for that could be the single shear processing direction without rotating the sample generated preferred orientation of crosslinks in material, and when this preferred orientation is parallel to the loading direction it cannot arrest or slow down the crack propagation.

![Figure 4.14: Effects of high shear processing direction on fracture toughness of MDF cements](image)

\( K_{lc} \) vs. shear processing direction
4.4.3 Effects of polymer hydrolysis degree on fracture toughness of MDF cements

The properties of PVAc are mostly controlled by their polymerization and hydrolysis degrees. Although polymer with high degree of hydrolysis show less moisture sensitivity, producing MDF with high hydrolysis degree polymers were unsuccessful, due to their low solubility at room temperature. Purpose of this study was investigating the effect of polymer hydrolysis degree on fracture toughness of MDF cements. Polymer with hydrolysis degree of 80%, 88%, 93% and 98.8% were used for this study. Water/cement ratio and polymer/cement ratio were kept same as mentioned in Chapter 3. It should be note that making MDF cements with the polymer has fully hydrolyzed (98.8%) were not successful, even the polymer was heated up before mixing. Thus, the fracture toughness was not measured for MDF cements with fully hydrolyzed polymer. Figure 4.15 shows the effects of polymer hydrolysis degree on fracture toughness of MDF cements. Considering the variations in sample preparation and fracture toughness testing, the hydrolysis degree of polymer does not have an obvious effects on the fracture toughness results. It was expected that the MDF cements made with lower hydrolyzed polymer has a higher fracture toughness value than that with higher hydrolyzed polymer.

![Figure 4.15: Effects of polymer hydrolysis degree on fracture toughness of MDF cements](image-url)
5. CONCLUSIONS AND RECOMMENDATIONS

The indentation-strength technique to measure the fracture toughness were found not effective to MDF cement due to the well-developed crack cannot be initiated, but two parameters fracture model were found applicable to MDF cements for measuring the fracture toughness. The typical fracture toughness was measured is about 1.79 MPa · m$^{1/2}$, and the Young’s modulus $E$ is about 42.8 GPa. Although the rapid decrease in strength immediately after peak load make it extremely difficult to initiate unloading at exactly 95% of the peak load, it provides an insight of fracture toughness of MDF cements and how to position the MDF cements in the brittle-ductile material system. Polymer with large particle size used for making MDF cement may not completely dissolve in water, and it may result low flexural strength. Polymer content in MDF cements do have a big impact on the flexural strength, but it does not affect the fracture toughness significantly. The changes on the hydrolysis degree of polymer in MDF cements does not affect the fracture toughness dramatically. Further research investigations on the direct relationship between the crosslink in MDF cements and its fracture toughness is recommended. Material characterization technique, such as microscopy, shall take to measure the degree of crosslink, and the toughing mechanism in MDF cements.
6. REFERENCES


