Optimisation of polymer concrete for the manufacture of the precision tool machines bases

By

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Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program.

Header Haddad
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Thank you
Publications

Published conference paper

Published journal paper

Abstract

One of the main operational drawbacks of the polymer concrete (PC) bases of precision tool machines is the high coefficient of thermal expansion (CTE). The non-uniform distribution of thermal expansion for the base under operational conditions induces high variation in the deflections on the base rails. The rails have direct contact with other mechanical components that hold the workspace in precision tool machines, impacting negatively on their accuracy. Reducing the CTE of the PC base to reach the CTE of the metal inserts (rails, pads, stands etc.) is essential to enhance the accuracy of the precision machine. Other parameters affecting performance directly such as damping ratio, flexural strength, moisture, dimethyl aniline (DMA) (promoter) and maturity need to be optimized to improve the PC used in the base of precision tool machines. In the present study, optimization of the PC base was undertaken according to the application requirements. The optimization process started with the optimization of the resin monomeric composition to lay the ground for further optimization of the PC aggregate composition. The optimization of both the PC resin binder and the composition of the aggregate were based on lowering the CTE and increasing both the flexural strength and damping ratio, since these properties are essential key controls for the thermal and mechanical stability of the bases used for precision tool machinery. Commercial unsaturated polyester (ARAPOL) resin was investigated along with other copolymers, methyl methacrylate (MMA) and styrene (St), in various proportions. The proportions of the resin monomer composition determine the thermal, mechanical and rheological properties of the resin. It was found that the optimum resin for use as a binder for PC base is 40% ARAPOL mixed with 60% MMA. In an effort to determine the optimum aggregate composition, six aggregates (basalt, river gravel, spodumene, fly ash, sand, and chalk) were investigated. PC samples were prepared with various aggregate
compositions containing the same resin volume fraction (aggregate 83% and resin 17%). Four-point flexural testing was utilized to measure the flexural strength of PC samples, and the CTE was measured using a custom-built device. The initial optimum composition with the highest flexural strength and lowest thermal expansion coefficient was found to be basalt, spodumene and fly ash. A basalt, sand and fly ash composition was nominated for further optimisation to reduce the resin volume fraction because of the ability of aggregate composition to adopt less resin. A reduction in the resin volume fraction (17% - 13%) in the PC reduces the value of CTE by 31% and flexural strength by 36%. This has no major effect on the PC base’s structural rigidity because of the large size of the base and the relatively small loads of the machine mounted on it. However, the damping ratio reduction is approximately 40%. This shortcoming can be overcome by increasing the structural damping properties of the whole machine. This can be achieved by installing a mechanical damper to the PC base to maintain the required damping ratio. The optimized aggregate composition was validated for the base of precision tool machinery using ANSYS 13.0 CAE software and comparing various aggregates compositions. Results show that the optimum composition offers more thermal stability and variation in the deformation of the base rails is reduced to negligible levels, which enhances the performance of the precision tool machine. The optimum composition (filler 87%, resin 13%) also offers the advantage of cost-effectiveness. The effects of the moulding temperature, mixing technology and the amount of DMA (promoter) on moulding were investigated, and the technology for mixing the resin with the aggregate was also investigated. Three mixing technologies were proposed and the optimum mixing technology nominated according to the level of mechanical strength of the PC sample. The effect of DAM amount (promoter) and the moulding temperature were investigated. An empirical relationship regulating the amount of DMA according to the moulding temperature was obtained. PC sample compaction was also investigated, and
various PC samples were subjected to a variety of frequencies for packing using a vibrating table. The optimum frequency is identified based on the mechanical strength of PC samples. The initial water (moisture) in the coarse aggregate of the PC composite components was studied, and a volumetric ratio of 1-5% water was included in the initial resin components. The effect of this water on the curing process, the CTE and the mechanical properties of both the resin and PC composites were investigated. It was found that moisture increases the curing time and the CTE for the resin binder, the PC composite, and the damping factor for the binding resin. It also decreases the flexural and compressive strength at various rates. A maturity study of the polymer concrete was conducted, under which the PC samples were cured at various temperatures for different periods of time. Flexural strength was measured for each time and temperature used for the curing. An empirical mathematical model describing the relationship between the relative flexural strength of PC and the curing time and temperature was obtained. In essence, this thesis has brought together the most essential aspects required to optimize polymer concrete for the manufacture of bases for precision tool machinery. These aspects relate to the PC composite material, polymeric binder, the effect of moisture on polymer and PC, mixing technology, maturity of PC, and moulding technology. All of these aspects were connected to the performance of the precision machine through the investigation of the material properties and the optimization process in accordance with the optimization criteria of the PC base used for the precision tool machinery. Results of this research showed improvements in these aspects and recommendations in terms of resin compositions, PC composition, DMA, manufacturing process were all adopted by the industrial partner.
Significant contributions of the thesis include:

- The optimization of the chemical composition of the binding resin to be used as a resin binder in polymer concrete. The purpose of the optimised resin is to use the most suitable binder when manufacturing bases for precision tool machinery according to the application requirements. The optimized resin binder produces the second lowest coefficient of thermal expansion (CTE), the highest damping factor, the highest flexural strength, the highest tensile strength, and the shortest curing time and is second in the ranking for level of hardness compared to other compositions.

- The nomination of the optimum aggregate composition for polymer concrete in order to provide the lowest CTE and an acceptable level of flexural strength within the application requirements.

- The development of an empirical relationship regulating the amount of DMA (promoter) according to the moulding temperature of the resin binder used in manufacturing the bases of precision tool machinery.

- The identification of the optimum frequency of the vibrating table for the PC sample to produce the maximum compaction based on the level of mechanical strength of the PC samples developed.
The provision of a fundamental understanding of all PC optimized parameters (damping factor, CTE, curing, flexural strength) and the main opposing parameter (moisture).

The optimisation of moulding technology in correlation with dimethyl aniline (DMA) (promoter) amounts and moulding temperature. Also optimisation of mixing technology within the consideration of aggregate morphology and on-going resin viscosity increase during the curing.

The implementation of a maturing method that enhances the productivity and the quality of polymer concrete for the base of precision tool machinery.

The development of interdependencies or relationships between mechanical properties such as flexural strength and the maturing time and maturing temperature, which can help to predict the flexural strength of polymer concrete within the curing time and temperature.

The conduct of an in-depth study of the effect of moisture on the CTE and mechanical properties, and on the curing behaviour of both resin and PC composite system.
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ATR-FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett, and Teller specific surface area and porosity</td>
</tr>
<tr>
<td>BJH</td>
<td>Barret, Joyner and Halenda theory to determine the desorption</td>
</tr>
<tr>
<td>BPO</td>
<td>Benzoil peroxide</td>
</tr>
<tr>
<td>CAD</td>
<td>Computer aided design</td>
</tr>
<tr>
<td>CAE</td>
<td>Computer aided engineering</td>
</tr>
<tr>
<td>CNC</td>
<td>Computer numerical control</td>
</tr>
<tr>
<td>CT</td>
<td>Computerised morphology</td>
</tr>
<tr>
<td>CTE</td>
<td>Coefficient of thermal expansion</td>
</tr>
<tr>
<td>DMA</td>
<td>Dimethyl aniline</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analyser</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>LDA</td>
<td>Logarithmic decrement analyses</td>
</tr>
<tr>
<td>MEKP</td>
<td>Methyl ethyl ketone peroxide</td>
</tr>
<tr>
<td>MMA</td>
<td>Methyl methacrylate</td>
</tr>
<tr>
<td>MRI</td>
<td>Magnetic resonance imaging</td>
</tr>
<tr>
<td>MT</td>
<td>Mixing technology</td>
</tr>
<tr>
<td>NRL</td>
<td>Natural rubber latex</td>
</tr>
<tr>
<td>NND</td>
<td>N, N-diethyl aniline</td>
</tr>
<tr>
<td>PC</td>
<td>Polymer concrete</td>
</tr>
<tr>
<td>SBR</td>
<td>Styrene-butadiene rubber</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TBS</td>
<td>Tertiary butyl catechol</td>
</tr>
<tr>
<td>TGA</td>
<td>Temperature gravimetric analysis</td>
</tr>
<tr>
<td>IAB</td>
<td>Interfacial adhesion bonding</td>
</tr>
<tr>
<td>TMPTMA</td>
<td>Terimethylo propane terimethacrylate</td>
</tr>
<tr>
<td>VV/VS</td>
<td>The ratio of void volume to sample volume in resin</td>
</tr>
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</table>
UPE Unsaturated polyester

**Symbols**

- $B_f$: Isothermal bulk modulus of the filler
- $B_m$: Isothermal bulk modulus of the matrix
- $D_1$: Biggest diameter of particle generations
- $D_2$: Smallest diameter of particle generations
- $D_3$: Intermediate diameter of particle generations
- $E_a$: Activation energy
- $G_m$: Shear modulus of the matrix
- $K$: The ratio of the biggest particle diameter and smallest particle diameter
- $K$: Rate constant for a single scanning in Brouchat model
- $M_c$: Maturity of concrete
- $M_{pc}$: Maturity of polymer concrete
- $n$: Reaction Order
- $R$: The gas constant 8.314 (J/mol °K)
- $S_i$: Specific surface area of aggregates
- $V_f$: Volume fraction of the filler
- $V_m$: Volume fraction of the matrix
- $V_p$: Packing factor
- $Z$: Pre-exponential factor
- $\alpha_f$: Coefficient of thermal expansion of dispersed filler
- $\alpha_m$: Coefficient of thermal expansion of matrix
- $\beta$: Coefficient of volumetric thermal expansion
- $\Delta H$: Heat Reaction
- $\delta_r$: Thickness of the resin layer
- $V_0$: The absolute volume
- $V_f$: Total volume fraction occupied by the solid particles
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1.1 Precision machines

A precision machine is a machine that performs a machining or non-machining process on a workpiece to a very high tolerance. The tolerance depends on the machine, the complexity of the workpiece and the stability of the work envelope. Precision machines can be classified into two categories: cutting precision machines and non-cutting precision machines. Precision cutting machines include computer numerical control (CNC) grinding tool machines, CNC milling machines, CNC turning centres, water jet cutting machines, laser cutting machines and ultrasonic machining centres. Precision non-cutting machines include magmatic resonance imaging MRI-machines, computerised tomography CT-scanners and metrology machines. All precision machines require ultra-stability for the workpiece envelope during operational conditions (Kim et al., 1995). Figure 1.1 shows a CT-scanner equipped with an enclosure made of polymer concrete (PC) for radiation protection and a PC base to enhance precision by damping the vibrations generated by the servomotors that control workpiece position and other servomotors operating on the workpiece.
The levels of vibration load, mechanical and thermal loads vary in precision machines, and depend on the precision machine’s functionality, capacity, stability and product complexity (Ema and Marui, 2003). A simple measurement for overall loads is the number of servo motors that a machine contains. For example, a CNC grinder tool machine has 5-7 servo motors operating at various speeds and located in different positions on the machine guided by 5 axes of motion, and in most production conditions operating at high speeds. It has a greater level of vibration compared to a CT-scanner, which contains only 2-3 servo motors operating at very low speeds for the sole purpose of moving and locating the workpiece (patient). The process of scanning 3-D images by CT-scanners would be more assured of sharp image acquisition in a vibration-free condition. This would assist in accurate patient diagnosis, and enable the scanning of non-patient work-pieces to the same level of image acquisition, thereby providing accurate data. A high level of accuracy can be achieved when the machine is equipped with a PC base. Here is
the magnitude of polymer concrete material used in the base of a precision machine to damp the unwanted vibrations accompanied with the operational condition to enhance the precision of the machine (Orak and Karademir, 2000).

1.2 Precision tool machines

The definition of a precision tool machine is elusive. There is no exact set of tolerance ranges that clearly defines a workpiece allowance limit when produced from a precision tool machine. A product considered high precision can range anywhere from having to consistently maintain a 5-micron tolerance for a large batch of parts, to maintaining a 2-micron, true positioning tolerance. This results when two parts accurately match up with each other (Techspex, 2008). This figure for understanding precision is not a constant level and can be changed depending on the time and assignment. One of the best applications in a precision cutting machine is the CNC grinding tool machine that evolved in terms of the precision level in accelerated steps. The demand for precision in tools has grown to such high levels to satisfy the growth in technology. This development has been continuous because of advanced manufacturing technologies for applications in the optical, automotive and communication industries, and especially in the medical and life sciences fields (Park, 2008).

The accuracy of precision tool machines depends on the stability level of the machine base-frame during operation. The stability level is affected by the subsystems mounted on the base that holds the workpiece, as well as on other subsystems that are responsible for conducting operations on a workpiece such as the cutting tool subsystem. Figure 1.2 shows a CNC grinding tool machine (ANCA, 2011). The positioning and cutting subsystems and their accuracy are
under complex dynamic and static internal loads in precision tool machines. These loads are generated from servo motors and other machine components, where forces, torques, vibrations and heat gradients are produced throughout the system to satisfy the grinding operation requirements.

In the meantime, these loads act as an error source because of their share in the thermal and dynamic stabilities in the workpiece envelope. Figure 1.3 shows the arrangement of a grinding wheel and the workpiece (tool) during a grinding operation. The machine has a special fixture that adds more stability to a relatively long workpiece for the purpose of gaining a better surface finish, a high level of precision and longer tool life (ANCA, 2009).
The main challenges for a CNC grinding tool machine are the geometric complexity (Tunc and Budak, 2012) and the high level of product surface finish for the workpiece, as these are vital precision requirements (Peter, 1965). Figure 1.4 shows tools with various geometries that can be manufactured by a CNC grinder tool machine. To satisfy these requirements, a workpiece should have a high level of stability throughout the manufacturing operation. The parameters affecting the grinding operation in terms of precision are: the material of the produced tool, the grinding wheel material, and the process control, such as the feed and speed of the grinding wheel and the tool’s complexity. Each of these parameters influences the precision level of the machine (Techspex, 2008).
1.3 The effect of level of precision tool on product accuracy in manufacturing sequence

A milling tool is a good example to demonstrate the effect of the level of tool precision on product accuracy through a manufacturing sequence. Once a milling tool is produced, it will then be used in a CNC milling machine to manufacture other products. Some of the products can be considered as tools for manufacturing a particular product. For example, a micro-injection mould (tool) can be used in producing micro-gears (product), which can be used in micro-fluid pumps, harmonic drivers, watches and medical equipment. Figure 1.5 illustrates the stages in the manufacture of plastic micro-gears. Micro-plastic gears eliminate noise due to the good damping properties of plastic. The noise was generated from the steel gears that were previously used in such applications. Other advantages of plastic gears are the ease of manufacture and the high productivity of the injection moulding process, which are reflected in the product life cycle of the gears, their high anti-corrosion resistance and precise control (Dopper et al., 1997).
Each process in the manufacturing sequence of the milling tool will have an influential effect on the precision of the micro-injection mould. The accuracy and functionality of the end product (for example, micro-plastic gears) will be affected by the accuracy of the post-process levels of the milling tool. In this case, micro-plastic gears inherit their level of accuracy from the original tool (milling tool) through the process of manufacture of the micro-mould. This depends greatly on the original milling tool produced by the CNC grinding tool machine and the milling machine used for the milling the micro-mould. The level of accuracy of both precision machines determines the accuracy level for all the products created, and hence the importance of a PC base for both the CNC grinding tool machine and the milling machine (Suh and Lee, 2008a). PC has a marked effect on the precision of the milling tool by damping the unwanted vibration created by servo motors during the manufacturing operation (Sezan, 2000).

Figure 1.5 Manufacturing the core of a mould, a micro mould for a plastic micro gear, and the steel micro gear.
1.4 Bases for precision machines

The bases for precision tool machines can be manufactured using different materials, including cast iron, polymer concrete (Lee et al., 2004), ferrocement (Rahman et al., 1987) and combined PC and ordinary concrete (Ding, 2010). The traditional material used in the manufacture of a CNC grinding tool machine base used to be manufactured using cast iron, but this did not fully satisfy the requirements due to the low damping ratio of cast iron, the inflexibility of the cast iron in terms of adapting internal plastic pipes, and the complexity in manufacturing, especially after the casting process. Ferrocement concrete and traditional concrete have a higher damping ratio than cast iron and PC has the highest (Rahman et al., 2001). PC is a composite material comprised of two kinds of constituents, namely well-graded inorganic aggregates and organic resin binder (ACI, 1986). A wide range of diversified thermosetting resins used as a polymeric matrix, namely epoxies, unsaturated polyester (UPE), polyureas, furan and polyurethane (Mosiewicki et al., 2009). Potential thermosetting resins to be used as a polymeric matrix in PC are including polysiloxanes, polyimides and polyglycols (Bucknall, 1992). Epoxies exhibit high strength, low shrinkage, and a relatively low coefficient of thermal expansion (CTE), and provide toughness as well as resistance to chemical and environmental damage (Michel, 2007). Unsaturated polyester provides excellent adhesive properties, a relatively lower strength than epoxy, a higher CTE and higher shrinkage than epoxy (Fowler, 2003). A wide variety of resins and aggregates has been used by various researchers to fabricate PCs. Epoxy as a binder is still used in PCs, but substantial research and engineering efforts have focussed upon cheaper vinyl monomers such as unsaturated polyester resin, methyl methacrylates (MMA), furan derivatives and styrene (Atta et al., 2005). There was a need for this research, which has optimized the properties of the polymeric matrix according to the optimization criteria for
the base of precision tool machinery as most of the preceding research was concerned with the resin as a material and did not connect the material fully with the application. In this thesis, consideration has been given to both the material and the application in order to reach the optimization.

Previous research on PC was more focused on the PC as a material and did not address the optimization criteria for a particular application fully to enhance the base of precision machine. There are some gaps, such as:

1. Optimization of the resin thermo-mechanical and rheological properties in accordance with the manufacturing process of PC and the final structural functionality of precision tool machine bases.

2. Nomination of the allowable moisture content in the fillers, based on the influence of water on the mechanical, thermal and rheological properties of the polymeric binder and the morphology of PC composite filler system.

3. Investigation of the effect of resin and filler volume fractions on the thermo-mechanical properties that affect the precision performance of the grinding tool machine. Investigation of properties such as CTE, damping characteristics and mechanical strength of the PC composite system.

4. Investigation of the effect of moulding technology, including the optimisation of mixing, maximum compaction and the vibrating time bias of the
rheological properties of the resin binder and morphological properties of the filler.

5. Identification of the amount of DMA according to the temperature-time dependant rheological properties of the polymeric binder and how it is going to affect the mechanical properties of the resin and PC composite.

6. Nomination of the maximum allowable moulding period based on curing studies and the temperature-time dependant, rheological properties of mortars.

7. Nomination of a maturing method compatible with the required mechanical strength of the base according to the optimization criteria of the grinding tool machine.

1.5  The replacement of cast iron by polymer concrete for bases of precision tool machines: advantages and disadvantages

The PCs used for manufacturing the bases of precision machines have numerous advantageous, including superior damping properties, manufacturing flexibility, fast curing, and good mechanical properties including high flexural and compression strengths. In addition, PCs have good adhesion for inserts, and are corrosion-resistant as well as cost-effective. Consequently, PC is a perfect replacement for cast iron (Bruni et al., 2008), which suffers from low damping properties, high cost, and low chemical resistance (Salje and Gerloff, 1986).
comparison of the properties of these materials and how they affect the manufacturing process and machine performance is discussed below:

**Damping ratio**: PC has a higher damping ratio compared to other materials. Cast iron has the lowest damping ratio compared to both PC and ordinary concrete (Rahman et al., 2001).

**Flexibility**: Hydraulic fluid (plastic pipes), tanks, threaded and non-threaded inserts, cutting fluids and conduit piping can all be integrated into a PC or a concrete base. Incorporating multiple components into one casting has a great impact on the reduction of assembly time. Multiple plastic components cannot be included in one casting of cast iron because the casting temperature is higher than the melting temperature of most plastic components (Salje and Gerloff, 1986).

**Melting temperature**: Cast iron requires a melting temperature of 1100 °C prior to casting and machining after casting. PC does not require any temperature rise during the process and no machining is required after curing.

**Cost**: PC and reinforced concrete materials are more cost-effective than cast iron as they contain 80-87% low cost aggregates (Chang and Stephens, 1975).

**Environmentally friendly**: PC and reinforced concrete bases do not require as much consumption of energy (Haddad et al., 1983) as cast iron for casting the base.
**Chemical corrosion resistance:** PC offers chemical resistance to most common solvents, acids, alkalis and cutting fluids. Cast iron and conventional concrete are susceptible to chemical corrosion under chemical attack (Gorninski et al., 2007).

**Stiffness:** PC has greater stiffness than concrete, and lower mechanical properties than cast iron (Cortes and Castillo, 2007), making it highly acceptable for the base of precision tool machines and fulfilling the application requirements.

**Water permeability:** PC has lower water permeability than cast iron and higher permeability than concrete.

The disadvantages of PC and concrete when used for manufacturing the bases for precision tool machines include the following:

**High non-uniform thermal expansion:** PC has a higher CTE because of the high CTE of the resin binder (Valore and Naus, 1975), compared to cast iron which has a low CTE. This condition leads to a non-uniform distribution of thermal expansion for the base during operation that induces a high variation in deflections on the base rails. This has a negative impact on the accuracy levels of precision tool machines.

**Low thermal conductivity:** PC has a lower thermal conductivity than cast iron, which has high thermal conductivity.

**Creep and shrinkage:** PC and reinforced concrete both have higher creep and shrinkage than cast iron (Haque and Armeniades, 1985).
Maturing time: PC requires longer maturing time compared to cast iron (Lee et al., 1997).

Machinability: Neither PC nor reinforced cement concrete can be machined, while cast iron has high machinability.

Cost: PCs are more expensive than conventional concrete materials (Cortes and Castillo, 2007).

1.6 Research objectives

The objectives of this research were as follows:

- Optimisation of the polymeric matrix based on its rheological properties and its mechanical and thermal characteristics. The optimization is in accordance with the manufacturing process of PC and the structural functionality of precision tool machine bases.

- Identification of the acceptable moisture content in the fillers, based on the influence of water on the mechanical, thermal and rheological properties of the polymeric matrix and the PC composite system.

- Optimisation of PC filler composition based on the manufacturing process of PC and the structural functionality of precision tool machine bases. Analysis of the effect of resin and filler volume fractions on the CTE,
damping characteristics and mechanical strength of the PC composite system.

- The material selection of the present research was based on cost, availability and the compatibility with the optimization criteria of PC precision tool machines base. The results will be compared to each other in accordance to the selection criteria, no need for benchmarking to be involved in result comparison.

- Development of moulding technology, including the optimisation of mixing and maximum compaction. Identification of maximum allowable moulding time based on curing studies and the temperature-time dependant rheological properties of mortars.

- Implementation of a maturing method, and determination of the interdependencies between flexural strength, curing time and temperature.

- Identification of the maturing time of PC and its dependence on environmental conditions.

1.7 Dissertation outlets

This thesis contains nine chapters as follows:

Chapter 1 – Introduction: This chapter includes an overview of precision machines, including precision tool machines and milling machines; how PC bases
have an essential role in the level of product accuracy; the inherited level of accuracy when the product of a precision tool machine is used in producing another product; and the advantages and disadvantages of the different kinds of materials used in manufacturing bases, such as PC and cast iron. The research objectives are also included in this chapter.

**Chapter 2 – Literature review:** This chapter contains a review of the relevant research and information about the properties of PC composite material in terms of binding resins and fillers, as well as a review of the use of PC in the manufacture of bases of precision machines such as CNC grinder tool machines.

**Chapter 3 – Materials specifications and testing methodology:** This chapter describes the experimental procedures, experimental set-up, the sample preparation methods and material specifications used in this research.

**Chapter 4 – Optimisation of polymeric matrix:** In this chapter the optimal chemical composition of the mortar is identified using resin’s thermal, mechanical and rheological properties as criteria of optimization. The manufacturing process and structural functionality of a precision tool machine base is also considered to categorise the optimization criteria.

**Chapter 5 – Optimization of polymer concrete composition:** In this chapter, various compositions of fillers (basalt, river gravel, spodumene, sand, fly ash, and chalk) are tested and the results discussed. The outcomes are compared with the
guidelines for optimization criteria in terms of the mechanical and thermal properties of the PC composite system. The preliminary optimum composition is identified. However, the second in the rank of PC composition is nominated for further optimization because of its volume fraction of filler and matrix. The final optimized composition is nominated, and validation of the final composition for the base of precision tool machines obtained. The validation reveals the effect of the aggregates composition and resin volume fraction of a PC composite on base behaviour, with regard to the accuracy level of the precision tool machine.

Chapter 6 – Optimization of moulding technology: This chapter shows how the moulding technology of PC that has low voids population and reproducible property is obtained. This includes the application of various frequencies during the packing operation of a PC sample. The mechanical strength was tested for each PC sample. The optimum vibration frequency to produce the PC sample that had the highest mechanical strength was chosen. Three mixing technologies were proposed and the optimum mixing technology nominated according to the level of mechanical strength of the PC sample. The relationship between DMA amount and moulding temperature and maximum moulding time is obtained, based on the rheological analysis of the resin binder.

Chapter 7 – Influence of moisture on thermal and mechanical properties and the curing behaviour of a polymeric matrix and PC composite system: This chapter describes how different volumetric ratios of water were included in the initial constituents of a polymeric matrix sample and water was induced in aggregates of a PC composite sample. The mechanical and thermal properties of the matrix and composite material of PC were tested, and the rheological behaviour of the polymeric matrix was examined. It was found that the existence of water results in
weaker mechanical properties and a slower curing rate for the resin and PC composite. The only property that improves is the resin damping factor as moisture increase, which is a negligible improvement compared to the shortcomings. The minimum limit for allowable moisture is identified. It is concluded that eliminating moisture to the minimal amount is crucial in order to maintain the quality and productivity of PC manufactured for precision tool machine bases.

Chapter 8 – Polymer concrete maturity study: In this chapter, PC samples were heated for various periods of time under different temperatures. PC samples were tested for flexural strength with different maturity conditions. The maturity method was identified and the datum temperature calculated. Mathematical expressions that predict the correlation of the relative flexural strength with maturing temperature as well as the time of maturing were evolved. It is concluded that an increase in temperature by ten times decreases maturing time by approximately 80%. The presence of moisture during the maturing process was investigated. It was found that the existence of water diminishes the resin mechanical properties by two or three times as the maturing temperature increases, compared with the effect of moisture at the ambient temperature.

Chapter 9 – Conclusions and recommendations for further research: Finally, in this chapter, conclusions and recommendations are drawn from this research. The chapter also highlights the limitations and deficiencies and proposes further work that could be undertaken to address these deficiencies.
Chapter 2

Literature review

2.1 Introduction

Polymer concrete (PC) is a composite material consisting of well-graded inorganic aggregates bound using a resin instead of the water and cement binder typically used in traditional cement concretes. The composite material of inorganic fillers combined with a binding polymeric resin with a liquid organic resin which hardens through the polymerisation reaction (Akihama, 1973; Andries, 1965; Ahn, 2004). Usually the binding resin is a thermosetting material curing irreversibly via cross-linking by radical initiation (Gawdzik et al., 2003). The thermoset polymeric binder in PC provides a matrix with high thermal, chemical and mechanical stability, making PC the material of choice for use as high precision tool machine bases.
2.2 Thermosetting material in polymer concrete

Thermoset is a polymeric material in which individual polymeric molecules have been joined through covalent bonds in specific regions on the molecules. Covalent bonds are generated by energetically exciting other polymeric molecules end groups, specific functional groups or by use of monomers (Gawdzik et al., 2003). The bonding of the molecules, also referred to as cross-linking, produces unique behaviour, such as a thermal stability that is much higher than that of thermoplastics. This condition arises because the rigidity of the macrostructure is maintained through links between the polymers that oppose the flow of molecules past each other. The mobility of molecules increases at higher temperatures due to an increase in the energy levels in the molecules, which results in greater material deflection. However, being one big macro-molecule, flow is not possible (Brunelle, 2008). Generally thermoset is maintained well under the thermal loads, the less notable are the reductions in mechanical properties due to any temperature increase. Other unique characteristics that make thermosets very attractive for many applications include their bonding capabilities, their strength, their thermal and damping characteristics, their chemical stability and minimal creep (Sidney, 1986). These physical and chemical properties rely on the processing conditions and on the cross-linking curing reaction that takes place during the process (Hanemann et al., 2010).

Thermoset material is used in a variety of applications such as paints and adhesives, and in the automotive, building and packing industries, among others. Thermosetting resins have been employed in this research project as a binding resin in PC in order to examine the mechanical, thermal and rheological properties of PC and the resin.
2.3 The use of thermoset material in polymer concrete research

The unsaturated polyester (UPE) resin used as a binder contain cyclohexanone peroxide as a catalyst and cobalt naphthaenate as an initiator (Strarmenov et al., 1965). A combination of methyl methacrylate (MMA) with UPE was also used in PC to examine PC’s mechanical properties (Slomatove, 1970). UPE was also utilized with MMA and terimethylol propane terimethacrylate (TMPTMA) as a binder in PC and tested for different mechanical properties at elevated temperatures.

A combination of UPE-MMA-styrene thermosetting resins was employed as a binder for the purpose of testing the mechanical properties of PC (Burleson, 1974). UPE was also used as a binder for PC where methyl ethyl ketone peroxide (MEKP) was the catalyst and cobalt octoate was the promoter (Ohama, 1973). In another study, PC containing poly-MMA-styrene resin was utilized to examine PC’s mechanical properties (Chang and Stephens, 1975). An investigation into the stress-strain relationship of PC containing UPE compared with two epoxies was conducted to examine the properties of PC containing different resin binders (El-Hawary and Abdel-Fattah, 2000). UPE was employed in another investigation in order to induce additives such as a silane coupling agent, TMPTMA, and divinyl benzene, which improved the properties of PC (Gorninski et al., 2004). UPE was also utilized to study the effect of mortar types (orthophtalic, isophthalic) on the strength degradation of PC in acidic environments (Dharmarajan, 1987, Gorninski et al., 2007).
It is interesting to explore the usage of UPE in PC when combined with various constituents and their effect on different aspects of PC’s mechanical, thermal and chemical properties. It is also important to consider other polymers involved as a thermosetting binder in PC, such as furfural-acetone and ureaformaldehyde. A combination of furfural (F) and furfural-acetone (FA) monomer (Andries, 1965) was employed as a mortar in PC, the proportion of F-FA being 1:7. In another study, furfural acetone (FA) was used as a resin binder (Davydov, 1972) and the PC’s mechanical properties examined. Elsewhere, furan resin was utilized as a resin binder in PC (Muthukumar and Mohan, 2004). In Alzaydi et al.’s (1990) study, ureaformaldehyde (UF) was utilized as a binding resin in PC to reduce the cost of PC which is the resin. It was concluded that the compressive strength of Portland cement concrete specimens is surpassed by that of ureaformaldehyde (UF)-PC for a similar binder volume fraction (ALZAYDI et al., 1990).

Another study used UPE produced from recycled PET, which makes it more attractive in terms of cost (Rebeiz 1996). The mechanical properties of PC containing UPE produced from recycled PET are lower than those for UPE made from virgin material. The UPE produced when using recycled PET may become suitable for manufacturing the PC base, if the application requirements is fulfilled by justify the structural design of the PC base and the aggregates composition of the PC towards fulfillment of the application requirements such as low CTE and high damping ratio, and this is a subject to future research outcomes. Structural wise it is suitable for manufacturing the PC base other related parameter need to be researched. It is also suitable for a construction application since it demonstrates a higher level of mechanical strength than conventional concrete.
Numerous researchers have investigated different kinds of epoxy resins as a binder for testing the mechanical and chemical properties of PC. Epoxy was used as a mortar in various proportions of epoxy resin to PC (Welch et al., 1962) to investigate its effects on the mechanical properties of PC. Epoxy was also employed as a binder in PC, where creep studied, and a mathematical model was developed to describe the creep behaviour in PC containing epoxy as a binder (Broniewski and Jamrozy, 1975). Other researchers have utilized epoxy as a binder in PC, investigating the effect of environmental temperature and NaOH concentration on corrosion behaviour, and the corrosion mechanism of epoxy and UPE in NaOH solution (Hojo et al., 1986, Reis, 2010). The effect of three freeze/thaw thermal cycles for 7 days on the strengths of the optimized PC was investigated experimentally and epoxy was used as the resin binder to find the level of thermal cycles which influence the mechanical properties of PC (Shokrieh et al., 2011).

### 2.3.1 The use of thermosetting binder in manufacturing PC base precision tool machine

A wide range of thermosetting resins can be used as a binder for the PC used in manufacturing the bases of precision tool machines, namely epoxies (Lu et al., 2006), unsaturated polyester (UPE), furan (Andries, 1965) and polyurethane (Michel, 2007). The most common thermosetting binders in PC are epoxies and unsaturated polyester. Epoxies exhibit high strength (Lau and Buyukozturk, 2010), low shrinkage, low coefficient of thermal expansion (CTE), and provide toughness as well as resistance to chemical and environmental damage in comparison to UPE (Kim et al., 1995).
Unsaturated polyester (UPE) provides good adhesive properties, relatively lower strength, a higher coefficient of thermal expansion and higher shrinkage than epoxy (Fowler, 2003). In addition, UPE is less expensive than epoxy and when MMA is involved in the composition of the resin, at the early stage the initial viscosity is low compared to epoxy (Vipulanandan and Paul, 1990), providing sufficient mixing to enhance the process of the aggregate-resin mixing. In addition, PCs containing poly methyl methacrylate (PMMA) as a binder showed a high modulus of elasticity (Mun and Choi, 2008) and a very low thermal coefficient of expansion (Blaga and Beaudoin, 1985), making MMA a good candidate to control and balance the rheological, mechanical and CET characteristics of the binding polymer in PC. The cost effectiveness, the potentially good thermal, mechanical properties and the good process for mixing aggregate and resin are the main drivers for research into UPE/styrene/MMA monomeric composition. The main function of thermoset material is the binding resin in the PC composite system for use in the bases of precision tool machines. The main reason for optimization of PC used in precision tool machine in this research is to elevate the precision level by inducing enhanced mechanical properties resin binder in the PC according to the application requirements. Also obtain a flexible and low cost manufacturing process of the precision tool machine PC base for further enhancement to the mechanical strength.

2.3.2 Unsaturated polyester and copolymers

In general, the UPE structure varies, being defined by the repetitive carbon-carbon double bond between carbonyl groups. UPE polymers have a number of average molecular weights within the range of 800-3000 units. A generalized representation of the UPE chemical structure is shown in Figure 2.1.
Styrene is another monomer used as it has the benefit of being low in cost. Styrene polymerize very actively with UPE at room temperature, show a higher rate of polymerization at elevated temperatures, and have low viscosity. Styrene’s chemical structure is shown in Figure 2.2.

Other applications utilise monomers that are used to induce the co-polymerization of UPEs. Their applications are shown in Table 2.1(Sidney, 1986).
Table 2.1 Examples of some non-styrene monomers used in UPEs.

<table>
<thead>
<tr>
<th>Monomer Application</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl methacrylate (MMA)</td>
<td>Enhanced weather resistance</td>
</tr>
<tr>
<td>Butyl acrylate (BA)</td>
<td>Enhanced weather resistance</td>
</tr>
<tr>
<td>Butyl methacrylate (BMA)</td>
<td>Enhanced weather resistance</td>
</tr>
<tr>
<td>Alpha methyl styrene (AMS)</td>
<td>&quot;Cooler&quot; cure, reduced exothermal</td>
</tr>
<tr>
<td>Vinyl toluene (VT)</td>
<td>Less volatility, higher flash point</td>
</tr>
<tr>
<td>Para-methyl styrene (PMS)</td>
<td>Less volatility, higher flash point</td>
</tr>
<tr>
<td>Octyl acrylamide (OAA)</td>
<td>Solid monomer, moulding compounds</td>
</tr>
</tbody>
</table>

Methyl methacrylate (MMA) is a low viscosity monomer, clear liquid that polymerises with UPE as a result of cross-linking in the presence of an initiator such as MEKP. Mixing MMA with UPE results in low viscosity resin at the early stage of curing which is enhanced the mixing performance of resin with the aggregates. In addition, PC containing poly (methyl methacrylate) as a binder showed high modulus of elasticity (Mun and Choi, 2008) and very low thermal coefficient of expansion (Blaga and Beaudoin, 1985). It also induces additional properties in PC such as fast setting and low temperature hardening (Ohama et al., 1981, Paul et al., 1973), leading to potentially good mechanical properties in PC bases containing UPE/MMA composition. Figure 2.3 shows the chemical structure of MMA.
When the initiator is added, a free radical is produced that can interact with the UPE carbon double bonds (C=C) and styrene molecules as well as MMA, creating new radicals (Gawdzik et al., 2003). These new free radicals can then react with other C=C double bonds, propagating the reaction and creating junctions that will result in a cross-linked network (Sidney, 1986). methyl ethyl ketone peroxide (MEKP) was used as an initiator and dimethyl aniline (DMA) as an accelerator to increase the curing rate (Gawdzik et al., 2003). Figure 2.4 shows the chemical structure of MEKP and Figure 2.5 shows the chemical structure of DMA.
Cobalt octoate can be used as a promoter to increase the activity of a given initiator (MEKP). The promoter helps in the decomposition of the initiator, delivering radicals at low temperatures by producing low-level activation energy for radicals to start the cross-linking, and initiates quickly. Figure 2.6 shows the chemical structure of cobalt octoate.

Figure 2.5 Chemical structure of DMA

Figure 2.6 Chemical structure of cobalt octoate (promoter)
2.4 Polymer concrete containing UPE-MMA as a resin binder

The addition of methyl methacrylate (MMA) to UPE has been investigated by Slomatove (Slomatove, 1970). The following observations were made: the addition of MMA to UPE provided an increase in weathering resistance, strength increased with time, and increase in shrinkage occurred in the polymer concrete using an MMA-UPE resin composition. The increase of shrinkage in MMA-UPE resin composition is due to the high shrinkage of UPE. In another study, a highly graded aggregate mixture with MMA-TMPTMA (terimethylol propane terimethacrylate) monomer was successfully designed. The PC was cured at 163 °C and tested at different temperatures, and the results are shown in Table 2.2 (Kukacka and Depuy, 1974).

<table>
<thead>
<tr>
<th>Testing temperature °C</th>
<th>Compressive Strength Mpa</th>
<th>Split Tensile Strength Mpa</th>
<th>Modulus of Elasticity Gpa</th>
<th>Poisson’ Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>-15</td>
<td>170.91</td>
<td>10.4</td>
<td>42.05</td>
<td>0.24</td>
</tr>
<tr>
<td>70</td>
<td>135.135</td>
<td>9.86</td>
<td>36.4</td>
<td>0.23</td>
</tr>
<tr>
<td>190</td>
<td>97.21</td>
<td>9.45</td>
<td>30.61</td>
<td>0.22</td>
</tr>
</tbody>
</table>

It was concluded that environmental temperatures greatly affect the mechanical properties of PC.
2.4.1 UPE produced from recycled PET used as a binder in PC

The purpose of utilizing polyethylene terephthalate (PET) waste is to reduce the high cost of PC which derives from the resin, and to dispose of the waste. Rebeiz investigated the strength properties of PC made using UPE made of recycled PET plastic (Rebeiz 1996). It was found that PC could develop 80% of its final strength in one day, with a compressive strength of 90 MPa and a flexural strength of about 20 MPa. The PC did not demonstrate a great loss in strength when tested at high temperatures, and remained quite strong in compression and flexure when compared to conventional concrete. Another study with a similar purpose investigated different parameters (Jo et al., 2008) such as strength and resistance to the acid and alkali compounds of PC, measured using differing coarse and fine aggregate ratios and resin content. It was found that the strength of PC made using UPE produced from recycled PET and recycled aggregate increases with increasing resin content. The stress–strain curves of PCs with 100% natural aggregate compared to 100% recycled aggregate exhibited different failure mechanisms. In relation to acid resistance, the polymer concrete at 9% resin was hardly affected by the Hydrochloric acid (HCl), whereas the PC containing 100% recycled aggregate showed poor acid resistance. Unlike acid, the contents of the alkali compounds did not seem to attack the PC with 100% recycled aggregate, as could be observed from the weight change and the compressive strength (Jo et al., 2008).

In a study conducted by Jo et al, both short-term and long-term creep models were developed incorporating various types of filler (CaCO3 and fly ash) (Jo et al., 2007). The difference between the proposed model and the experimental long-term creep compliance was less than 4%. The creep strain in the early stages increases in PC more rapidly than in ordinary concrete. The creep strain of PC without filler...
was much higher than that of PC with filler CaCO3, which was more effective than fly ash. The creep values increased with an increase in applied stress, although the values were not proportional to the stress ratio, because of the nonlinear viscoelastic behaviours of recycled PET in polymer concrete (Jo et al., 2007). This result is partially consistent with the results of (Mahdi et al., 2007), specifically in relation to the effect of resin volume fraction on mechanical strength.

In similar research, Reis (2011) utilized PTE as aggregate and the mechanical properties were measured. The fracture properties of PC composites were investigated by adding shredded PET as filler, employing UPE and epoxy as a resin binder individually. Both resin binders (UPE and epoxy) were produced from virgin material (Reis, 2011). Shredded PET was used as a partial substitute for natural fillers. The ratios of induced PET in the PC filler composition were 5%, 10%, 15% and 20% by weight. It was observed that a reduction of a specific weight resulted as the PET filler ratio increased. As the PET content rose through each test series, the PC material became more ductile and showed less brittle failure. Any level of shredded PET adversely affected the fracture toughness and elasticity modulus in both epoxy and UPE mortars. This improvement occurred in the fracture energy for both epoxy and UPE polymer mortars when shredded PET aggregates were added to the mixture as a substitute for natural filler. This substitution produced a PC composite with high energy absorption that could be used for structures under dynamic and impact conditions (Reis, 2011).

(Mahdi et al., 2010) conducted another investigation with a similar focus where parameters such as PET-glycol ratio, dibasic acids and initiator promoter combinations were studied, and their effects on mechanical properties, such as the
The compressive stress of the UPE produced from recycled PET were investigated. The UPE produced by using recycled PET plastic waste was depolymerised through glycolysis. The initiator promoter combinations used were methyl ethyl ketone peroxide (MEKP) and cobalt naphthaenate (CoNp) in one group of sets, and benzoil peroxide (BPO) and N, N-diethyl aniline (NNDa) in the other group, as shown in Table 2.3 for each set. The compressive strength of resin and PC produced with MEKP as the initiator is more than the compressive strength of resin and PC produced with BPO initiator (Mahdi et al., 2010). The compressive strength of resin as well as PC produced with a PET to glycol ratio of 2:1 is usually more than that of 1:1. The resin and PC produced with a PET to glycol ratio of 2:1 used malie and phthalic anhydride as diabasic acids and MEKP and CoNp as initiator and promoter produced a high compressive strength. The split tensile strength of PC is either equal to or more than the tensile strength of the equivalent grade of cement concrete. It was concluded that set numbers 1, 2, 5 and 6 were better than the rest in terms of compressive strength, split tensile strength, morphology of the material and thermal stability as shown in Table 2.3 for each set. The compressive strength of resin and PC produced with MEKP as the initiator is greater than the compressive strength of resin and PC produced with BPO initiator (Mahdi et al., 2010). The compressive strength of resin and PC produced with a PET-to-glycol ratio of 2:1 is usually more than 1:1. The resin and PC produced with a PET-to-glycol ratio of 2:1 used malie and phthalic anhydride as dibasic acids and MEKP and CoNp as initiator and promoter produced a high compressive strength. The split tensile strength of PC is either equal to or more than the tensile strength of the equivalent grade of cement concrete. It was concluded that set numbers 1, 2, 5 and 6 were better than the rest in terms of compressive strength, split tensile strength, morphology of the material and thermal stability as shown in Table 2.3 (Mahdi et al., 2010). These various results are important for establishing future research for PC precision machine bases.
employing UPE produced from recycled PET that may accommodate the application requirements. The most important parameters that need to be investigated are the damping ratio and CTE of the binding resin as well as the PC composite system.

Table 2.3 Different combinations of PET-to-glycol ratio, dibasic acids and initiator promoter for UPE made from PET waste (Mahdi et al., 2010).

<table>
<thead>
<tr>
<th>Set</th>
<th>Chemical combinations of UPE made of recycled PET</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Group – I</td>
</tr>
<tr>
<td></td>
<td>Dibasic acid malic anhydride and phthalic anhydride</td>
</tr>
<tr>
<td></td>
<td>Initiator Benzoil peroxide, promoter N, N-diethyl aniline</td>
</tr>
<tr>
<td></td>
<td>PET-to-glycol ratio 1:1</td>
</tr>
<tr>
<td>2</td>
<td>PET-to-glycol ratio 2:1</td>
</tr>
<tr>
<td>3</td>
<td>Group – II</td>
</tr>
<tr>
<td></td>
<td>Dibasic acid malic anhydride, Initiator benzoil peroxide</td>
</tr>
<tr>
<td></td>
<td>Promoter N, N-diethyl aniline</td>
</tr>
<tr>
<td></td>
<td>PET-to-glycol ratio 1:1</td>
</tr>
<tr>
<td>4</td>
<td>PET-to-glycol ratio 2:1</td>
</tr>
<tr>
<td>5</td>
<td>Group – III</td>
</tr>
<tr>
<td></td>
<td>Dibasic acid malic anhydride and phthalic anhydride</td>
</tr>
<tr>
<td></td>
<td>Initiator methyl ethyl ketone peroxide (MEKP)</td>
</tr>
<tr>
<td></td>
<td>Promoter cobalt naphthanate (CoNp)</td>
</tr>
<tr>
<td></td>
<td>PET-to-glycol ratio 1:1</td>
</tr>
<tr>
<td>6</td>
<td>PET-to-glycol ratio 2:1</td>
</tr>
<tr>
<td>7</td>
<td>Group – IV</td>
</tr>
<tr>
<td></td>
<td>Dibasic acid malic anhydride</td>
</tr>
<tr>
<td></td>
<td>Initiator methyl ethyl ketone peroxide (MEKP)</td>
</tr>
<tr>
<td></td>
<td>Promoter cobalt naphthanate (CoNp)</td>
</tr>
<tr>
<td></td>
<td>PET-to-glycol ratio 1:1</td>
</tr>
<tr>
<td>8</td>
<td>PET-to-glycol ratio 2:1</td>
</tr>
</tbody>
</table>
2.4.2 Improve the damping properties of UPE polymeric matrix

When a rubbery phase is introduced into a polymeric matrix, the mobility of the rubber molecules enhances the dissipation of vibration energy in the resin domain (Cherian and Thachil, 2003, Pachpinyo et al., 2006). Synthetic and natural rubbers and elastomers in solid and liquid forms have been applied to improve UPE damping properties. Rubbers such as natural rubber latex (NRL) (Pachpinyo et al., 2006) and styrene-butadiene rubber (SBR) (Ray, 2008), and functional elastomers such as hydroxyl terminated polybutadiene, epoxidized natural rubber, hydroxyl terminated natural rubber, and maleated nitrile rubber (Cherian and Thachil, 2003) have been used to enhance UPE damping properties. Polyoxypolylenetriamine (POPTA) was employed combined with temperature during curing to optimize the damping factor and mechanical properties of UPE (De La Caba, 1999). In addition polyhedral oligomeric silsesquioxanes (EA-POSS) was used to improve the damping behaviour and other mechanical properties of UPE (Gao et al., 2009). These modifications increased the toughness and tensile strength of the UPE resin. The dissimilarity of the rubbery and resin phases results in miscibility problems which researchers have attempted to solve using copolymerizing terminal groups (Maspoch and Martinez, 1998) and dispersants and solvents (Pachpinyo et al., 2006). Copolymers of UPE and polyurethanes (Cherian et al., 2006), polyureas, polysiloxanes, polyimides or polyglycols also produce resins with improved damping properties (Bucknall, 1992).

Butadiene as vinyl monomer has also been employed to modify UPE resin’s mechanical properties for the purpose of improving the damping properties of UPE (Rodriguez, 1993). Including a rubbery phase into a polymeric matrix of PC base by inducing materials such as NRL and SBR could increase the CTE of the resin binder. This may resulted into increase the CTE of PC base of precision tool
machine which has a negative impact on the accuracy level of the precision tool machine.

2.4.3 Effect of curing on mechanical properties of UPE

Curing and processing conditions also have a significant effect on UPE mechanical properties. The literature suggests that varying the resin curing rate via the curing temperature or the initiation mechanism or post-curing heat treatment of the resin affect the UPE damping properties (Liu et al., 2002).

Li et al. (2004) studied the effect of high temperature curing and post-curing heat treatment on the micro-heterogeneity of UPE and its effect on its mechanical properties (Li et al., 2004). Kim et al. (1995) used UV initiation curing UPE and found that the type and the amount of photo initiator affects the level of improvement in mechanical properties (Kim et al., 1995). Sanchez et al. (2000) showed that the styrene ratio in the UPE pre-polymerization mixture affects the phase continuity of resin after curing due to the limited miscibility of polystyrene in UPE (Sanchez et al., 2000). This phase separation can be affected dramatically by curing temperature (Zheng et al., 1988).
Fillers in polymer concrete

Fillers occupy 80-85% of PC and they form the mechanical properties of the PC, depending on filler proportion, the morphology of the aggregate, the particle size distribution and the mechanical and thermal properties of the fillers. Different kinds of fillers are used for PC that can be classified as natural and non-natural. The main purpose of investigating a single filler or group of fillers is to enhance a single mechanical or thermal property or group of mechanical and thermal properties in a PC. The most common combination of aggregates is basalt, river gravel, sand and chalk (Ohama, 1979, Burleson, 1974, Atta et al., 2005). Fly ash has been employed in PC as filler in various research studies, as it enhances PC’s mechanical properties (Semiha and Cengiz 2011, Demirboga and Gul, 2003, Varughese and Chaturvedi, 1996). Portland cement Type II has been used as a filler in PC for the purpose of improving PC’s mechanical properties (Tolbert and Hackt, 1979). Siliceous aggregates, ground chopped glass and graded round iron have been included in PC as fillers (Brocard and Cirrode 1967). PET waste has been utilized as a filler as a way of recycling this material effectively (Reis and Carneiro, 2011). Trap rock was employed as a filler in PC produce a higher strength PC than other types of aggregate and Type I cement enhances the strength considerably when replacing gypsum (Helal, 1978).

Effect of fillers on polymer concrete properties

The filler have a great effect of mechanical properties of PC composite system because filler morphology forms the interfacial bonding and the adhesive of binding resin with aggregates. In addition the fillers morphological, thermal and mechanical properties have an effect of PC thermal, mechanical properties. The use of siliceous aggregates, ground chopped glass and graded round iron was
investigated as fillers for PC (Brocard and Cirrode 1967). It necessitated a higher resin volume fraction of 15% due to an increase in the surface area of the aggregates, a compressive strength of 85 MPa, a modulus of rupture 16.69 MPa, a dynamic modulus of 28.24 GPa and a static modulus of elasticity of 18.24 GPa. The coefficient of thermal expansion (CTE) was $22 \times 10^{-6} \, ^\circ \text{C}^{-1}$. Shrinkage and water absorption were minimal. The aggregates as filler have not been used since the results demonstrated that the addition of non-natural aggregates failed to improve the strength. Upon examining the results obtained when employing this group of fillers, it was reasonable to claim that the those kinds of fillers are not suitable for manufacturing a PC base for precision tool machine due to high CTE and low mechanical strength.

Ohama (Ohama, 1979) conducted another filler study, four coarse aggregates were used to prepare PC samples to be tested for compressive strength using UPE as a mortar. Each sample showed different results for compressive strength when the volume fraction of coarse aggregates was varied. It was found that increasing the compressive strength of coarse aggregates tends to increase the compressive strength of polymer concrete (Ohama, 1979) and that increasing the volume fraction of coarse aggregates tends to decrease the compressive strength of polymer concrete.

In another study, shrinkage-free PC was achieved by dispersing small amounts of the mineral montmorillonite into the resin (Haque and Armeniades, 1985). It was found that the resin interacts with the hydrated mineral, creating expansion forces, which counteract epoxy resin shrinkage. It was concluded that the addition of 0.2% of montmorillonite or less produced shrinkage-free PC composite systems with a flexural strength 30% greater than the corresponding conventional PC. A
higher level of montmorillonite content created PC systems that expanded upon
curing or generated hydrostatic pressure during a constant-volume cure (Haque
and Armeniades, 1985). Montmorillonite filler could contribute to a shrinkage-free
PC base, but it is not available in Australia, making montmorillonite quite costly.

In another filler-focused study fly ash was introduced to PC as fine filler, granite
was used as a coarse aggregate, and river sand was the middle-sized aggregate.
The binder was epoxy and PC properties such as cure time, flexural strength and
resistance to water absorption were compared with PC containing river sand
(Varughese and Chaturvedi, 1996). Flexural strength, curing time and resistance of
water absorption were measured for both the fly ash samples and the river sand
samples. It was concluded that fly ash could be used as a fine aggregate to
partially or fully replace ordinary river sand in PC systems. The flexural strength
of PC was improved as the fly ash weight fraction increased. PC containing fly ash
needed a slightly shorter time to cure than the PC containing river sand. When fly
ash was increased to just below 50%, water absorption was equal to that of PC
containing river sand (Varughese and Chaturvedi, 1996).

Rebeiz et al. (2002) conducted a further study, in which fly ash was investigated as
a replacement for sand in PC (Rebeiz et al., 2002). It was demonstrated that the
replacement of 15% by weight of sand with fly ash improves the compressive
strength of unreinforced PC cylinders by about 30% and the flexural strength of
steel-reinforced PC beams by about 15%. Other improvements in properties were
relatively minor and included the tensile bond strength of PC under thermal
cycling and the creep compliance of the PC under sustained loading. This may be
because fly ash achieves better workability than sand. The morphology of the
particles is fine and the spherical particles of fly ash provide the fresh PC mix with
improved lubricating properties. The use of fly ash may also produce optimum packing conditions for the different ratios of sand and fly ash during casting, thus resulting in a more homogeneous and compact final PC product. The replacement of sand with fly ash did not have an impact on the shear strength of PC (Rebeiz et al., 2002).

Sofi et al. (2007) investigated numerous aggregate compositions in an effort to assess the effects of the inclusion of coarse aggregates and granulated blast furnace slag into a polymer composite system (Sofi et al., 2007). The engineering properties of inorganic PC (referred to by the authors as IPC) include the modulus of elasticity, Poisson's ratio, compressive strength, splitting tensile strength and flexural strength, which were then compared with organic polymer concrete (referred to by the authors as OPC). All tests were executed according to the relevant Australian Standards. It was observed that for an IPC density similar to OPC-based concretes, the average compressive strengths of IPC for different compositions were sufficiently close to the design strength, with a mean of 52.4 MPa. The difference between the splitting tensile and flexural strength of the IPC mixes was approximately 2.0 MPa. An evaluation of the static modulus of elasticity of the IPC mixes was compared predominantly with models reported for higher strength concretes. It was found that, similar to OPC-based concrete, most mechanical properties depend upon the mix design and curing method (Sofi et al., 2007). The results reported for this research were considered by the researchers to be preliminary to long-term experimental work in the field of IPC. The researchers advised that further research would be carried out in future using mix compositions, including coarse aggregates with or without granulated blast-furnace slag to reinforce the validity of the research (Sofi et al., 2007).
Barbuta et al. (2010) investigated the effect of fly ash on compressive strength, flexural strength and split tensile strength. The results showed that the influence of fly ash and silica fume contents on the mechanical properties of PC containing epoxy resin as a binder was positive (Barbuta et al., 2010). The filler improved the mechanical characteristics of PC compared to that of polymer concrete without the investigated filler. The effect of variations in the filler compositions (100, 150, 200%) of silica powder and variations in epoxy resin (10, 15 ad 20%) on the mechanical properties of PC was investigated. Compressive, flexural and tensile strengths were tested. PC samples with 15 and 20% epoxy resin and 200% filler (15% fine silica powder, 25% medium size silica powder and 60% coarse silica powder) had maximum mechanical strengths. The values of compressive, flexural and tensile strengths were 128.9, 22.5 and 16.2 MPa respectively (Barbuta et al., 2010).

2.6 Properties of polymer concrete composite system

Flandro (1960) initiated the research into providing an alternative material to Portland cement in concrete as a paster, which is PC resin. Numerous mixes and curing procedures were investigated, using polyester resin as a binder (Flandro, 1960). A modulus of rupture of approximately 5.515 MPa and a compressive strength of 110.316 MPa were achieved with the optimum mix resin weight of 267.55 kg resin per cubic meter. Oven cured at 176.6 °C. In a similar study, the epoxy was used as paster in PC for various proportions of epoxy resin (Welch et al., 1962). Different volume fractions of epoxy resin were sampled using ¾ basalt to sand as an aggregate composition for PC. The best result was accomplished with the epoxy resin at 15% volume fraction. A compressive strength of 76.87 MPa, and a modulus of elasticity of 32.267 GPa were achieved when cured at
ambient temperature for 28 days. PC using UPE resin as a binder has also been studied (Strarmenov et al., 1965). The aggregate was fine silica and sand. The resin volume fraction was 16%, containing cyclohexanone peroxide as a catalyst and cobalt naphthaenate as an initiator. The following results were obtained: the PC was sampled using 7×7×7 cm cubic moulds, and cured for 3 days. The compressive strength achieved was 117.6 MPa and the flexural strength was 33.8 MPa.

Knab (1969) studied the discrepancy of load rate on the behaviour of polyester concrete studied for both the long and short term (Knab, 1969). A mathematical model was developed for the purpose of predicting long-term deflection. Significant deformation occurred under both long and short-term loading, which indicated a limitation on the use of polymer concrete in construction. Another study where the PC was composed of 7-8% FA monomer, 1.5-2% benzene acid, 55-57% granite chippings, 24-25% quartz and 9-10% micro filler (Andries, 1965). The following results were obtained from the experimental PC: specific weight was 2.19-2.5 g/cm³, compressive strength was 67.56-96.52 MPa and tensile strength was 2.19-2.5 MPa. A temperature variation test for 300 cycles between -30°C and 80°C showed a reduction in compressive strength of PC 50%-40% and 80%-85% in tensile strength. Based on those results the PC containing a combination of furfural (F) and furfural-acetone (FA) monomers suitability for manufacturing the PC base of precision tool machine is subject to the investigation of application requirement such as CTE flexural strength and damping properties. The compression strength and tensile seem to be acceptable. A particular modification on the structural design of the frame and the PC base precision tool machine also further reinforcement is required for the same purpose. This procedure is to
accommodate the high deflection in long and short term loading and low mechanical properties of PC consist of FA as a resin binder.

Burleson (1974) investigated unsaturated polyester UPE-MMA-styrene thermosetting resin as a binder for PC for different aggregate grading (Burleson, 1974). Various resin proportions were added to fire retardants, until the optimum mix was reached. Samples were cured at room temperature for 24 hours. Fine sand was used as aggregate and the compressive strength was 145 MPa. The flexural tensile strength was 32.61 MPa and the flexural modulus of elasticity was 10.06 GPa. The resin weight percentage was 20%. Using a larger-sized aggregate (maximum size 12mm) and 8.3% resin weight percentage, the compressive strength was 47.118 MPa, the flexural tensile strength was 14.3 MPa and the flexural modulus of elasticity was 19.02 GPa. It was concluded that the PC was cost-effective because of the low percentage of resin, which is the most expensive ingredient.

Ohama (1973) performed another investigation where the mechanical properties of polymer concrete were examined. The binder used was UPE. MEKP was the catalyst and cobalt octoate was the promoter. The mix design included a resin weight of 22.5%, 29.1% of 5-20 mm gravel, 9.5% of 1.2-5 coarse river sand and 83.8% of fine sand. Samples were cured at room temperature for one day, soaked with water for six days, and then left at room temperature for seven days. The outcome was the same strength regardless of the curing condition. Compression strength and split tensile strength were 98 MPa and 9.8 MPa respectively (Ohama, 1973).
Chang and Stephens (1975) conducted a study in which the mechanical properties were investigated of PC containing MMA-styrene monomers, with sand and gravel as aggregates, the focus of the study was the creep Type I cement was used as filler. The optimum resin content was 9% weight percent. The curing took place at room temperature for four hours. The highest compressive strength was 106 MPa, the flexural strength was 24.5 MPa and the split tensile strength was 10.755 MPa. Under 10-20% of compression strength, creep was measured. Creep increased as the resin percentage increased. The increase of temperature also increased the creep, particularly at 40°C the creep increased sharply. Below 40°C, creep increased almost linearly with stress (Chang and Stephens, 1975).

Another study by Suzuki (1975) used a fire test on PC containing UPE; the model dimensions were 1.52 × 1.85 × 3.2 m. No fire retardant was added to the resin. Wall and floor thicknesses varied between 8-3 cm, the fire load used was 13 kg/m², which is less than average in an ordinary building. A temperature of 500°C was recorded after 8.5 minutes, yet no structural damage occurred. Another fire load was tried with 24 kg/m². Tests resulted in some cracks occurring on the surface of the wall, yet no collapse occurred. At a load of 35 kg/m², heavy sooty smoke was released. The temperature reached 1000°C after 9 minutes and the walls caught fire. The model collapsed after 29 minutes. Introducing Dawsonite fire retardant did not improve the fire resistance (Suzuki, 1975).

Flame resistance of PC has also been tested (Prin and Cubaud, 1977). The flame was originally from a propane-oxygen burner with a discharge of 5m³/hr located 20 cm below the shell with a circular fan of 80 cm in diameter and a temperature of 3000°C. The gel coat burned instantly and ten minutes later the concrete started burning, but only above the flame. The silica aggregates decomposed but the face
opposite to the exposed surface did not heat up. After half an hour, the
temperature on the opposite face had risen to 10°C above the ambient
temperature. One hour later it accelerated to 30°C. As evident in the experiments,
resistance to flame was elevated and the heat propagation through the PC was
delayed. This research on fire was valuable since it provided a figure for a PC base
of a precision machine when under fire.

Hojo et al. (1986) investigated the effect of temperature and NaOH concentration
on corrosion behaviour; the corrosion mechanism of epoxy and UPE resins in
NaOH solution. Resins researched in this study were two types of epoxy: phenol-
A hardened with methyl-tetrahydrophlic (MTHPA), and epoxy using the same
base with 1.8-p-mentandiamne (MDA) as a hardener and isophthalic unsaturated
polyester. Epoxies and unsaturated polyester resins were immersed in NaOH in
different concentrations for different temperatures. It was found that epoxy resin
hardened with MDA demonstrated no degradation during the immersion because
of its stable crosslink. Epoxy hardened with MTHPA demonstrated a uniform
corrosion with the dissolution of the surface. Increasing the temperature increased
the corrosion penetration through the resin. PC containing UPE was corroded
with colour conversion and the resin surface softened like rubber (Hojo et al.,
1986). The rate of corrosion could be controlled by diffusion of the solution
through the resin surface. The corrosion mechanism was similar to the metal
corrosion. A formula for predicting the strength of resin after immersion was
developed, consisting of the effect of temperature and the concentration of NaOH
solution by applying the corrosion rate.

C. Vipulanandan and Eliza Paul (1990) studied the behaviour of epoxy and
polyester PC when applying various curing temperatures (22 and 120
°C)(Vipulanandan and Paul, 1990), and the influence of aggregate sizes and distribution on the mechanical properties of PC when the strain rate was varied between 0.01%-0.6% per minute. It was found that the gap-graded aggregates produce polymer concrete with better mechanical properties. The behaviour of both PC epoxy based and PC polyester based are definitely influenced by the curing condition and testing temperature.

In another study by C. Vipulanandan and Eliza Paul (1993), they studied the compressive and tensile properties of polyester polymer and polymer concrete under various curing conditions, temperatures, and strain rates. The curing temperature was varied from room temperature to 80°C. The strain rate was varied between 0.01% to 60% strain per minute and the temperature between 22°C and 120°C (Vipulanandan and Paul, 1993). It was concluded that the optimum curing conditions for polymer and polymer concrete were different. The strength, failure strain, modulus, and stress-strain relationship of polyester polymer and polymer concrete were also influenced by the curing method, testing temperature, and strain rate to varying degrees. The influence of test variables on the mechanical properties of polymer binder and polymer concrete was quantified. Pre-treating the aggregates with a silane coupling agent further enhanced the compressive and tensile strength of the polymer concrete. (Vipulanandan and Paul, 1993).

Czarnecki, L. et al. (1999) investigated the thermo mechanical properties of PC containing polyester and epoxy as a polymeric binder, and the statistical evaluation of the heterogeneity of polymer concrete was presented. It was found that a material model based on quadratic functions formed a suitable basis for the optimization of polymer concrete (Czarnecki, 1999). A comparison analysis of the
material models of the two main types of polymer concrete, epoxy and polyester concrete, was also conducted. The overall desirability function was then used as the metric for the multi-criteria optimization of polymer concrete. This optimization process was applied to several PC composites, including polyester concrete with silica fume, highly-filled polyester concrete that reduces material costs, and epoxy concrete with low flammability and combustibility. Experimental validation of the results of the optimization process was also conducted. It was found that compressive strength, flexural strength, and the modulus of elasticity were almost the same for both polyester concrete, epoxy concrete and, surprisingly, CTE. The research done for this thesis does not agree with these results (Czarnecki, 1999).

While it is important to explore the literature in terms of the mechanical and chemical properties of PC, it is also interesting to review the moisture effect and how to deal with it in PC. Ahn (2004) performed an investigation in which the mechanical properties of PC made with wet aggregates was improved (Ahn, 2004). Zinc dactylate (ZDA) and calcium dactylate (CDA) were each used as an additive to the resins (two epoxies). The variables were the amount of dactylate monomer and the aggregate conditions (wet or dry). The compressive strength, flexural strength, workability, working time, and curing time were measured. ZDA was found to improve the workability. The working time and CDA were also found to improve the compressive and the flexural strength when the PC mix had wet aggregates (Ahn, 2004).

The moisture sensitivity of UPE and acrylic PCs with commercial metallic monomer powders have been evaluated (Ahn, 2006). PCs containing different levels of these powders were investigated with respect to the properties of
hardened PC. The mix design was optimized for workability and strength, depending on the resin viscosity, the intended use and the additional quantities of the polymeric materials. The properties investigated included the compressive and flexural strengths of hardened PC. These polymeric materials offer the possibility of using wet aggregates in polyester and acrylic PC construction. It was concluded, after conducting a number of experiments, that the resistance to moisture was improved substantially with the addition of ZDA and CDA. Aggregate at a 0.5% moisture level with the addition of 5.0% of ZDA demonstrated an increase of 122% in the flexural strength and 50% in the compressive strength. At a 0.5% moisture level and with the addition of 5.0% CDA, increases of 38% in the flexural strength and 11.7% in the compressive strength over the control were obtained for the MMA-based PC system. The remarkable increase in strength indicates that ZDA and CDA may allow for the possibility of using wet aggregates in PC construction (Ahn, 2006). This research may be essential in a situation where wet aggregates are used in the manufacture of a PC base. ZDA and CDA are both very costly to implement in a production environment where it is necessary to reduce the cost of manufacturing PC bases.

Gorninski et al. (2004) examined the modulus of elasticity of PC compounds manufactured using two types of binders: orthophtalic or isophtalic UPE (Gorninski et al., 2004). The compositions used were selected from the available literature on PC compositions. Based on those data, the polymer concentrations used were 12% of orthophtalic UPE and 13% of isophtalic UPE by weight of dry materials. Fly ash was used as filler and compositions with 8%, 12%, 16% and 20% of ash by weight of aggregate were studied. Statistical analysis of the data revealed that the type of resin and the concentration of fly ash, both individually and in combination, have a significant effect on the modulus of elasticity of PC.
The effect of UPE type (orthophthalic, isophthalic) and micro-filler fly ash concentration levels on the strength degradation of PC in acidic environments has also been investigated (Gorninski et al., 2007).

Shokrieh et al. (2011) investigated the effect of three freeze/thaw thermal cycles on optimised PC. The criteria for optimization were epoxy resin weight fraction, chopped glass fibre and percentage aggregate size for the highest compressive and flexural strength that gained. The effect of three freeze/thaw thermal cycles: 25 °C to 30 °C (cycle-A), 25 °C to 70 °C (cycle-B) and -30 °C to 70 °C (cycle-C), applied for 7 days on the strengths of the optimized PC was experimentally investigated. A comparison was made of the experimental results for the mechanical strengths measured at room temperature. It was found that heating and cooling cycles did not influence the compressive strength of the optimally-designed PC. On the other hand, the bending strength was more influenced by exposing PC to thermal cycle-B (Shokrieh et al., 2011).

Weena Lokuge and Thiru Aravinthan (2013) investigated the mechanical properties of PC composed of three types of resin (polyester, vinyl ester and epoxy resin) when combined with different proportions of fly ash and sand. Three types of resin (polyester, vinyl ester and epoxy resin) were combined with fly ash and sand to make the organic polymer concrete mortar (Lokuge and Aravinthan, 2013). The effect of the polymeric binder, sand and fly ash contents on the compressive strength, flexural strength, split tensile strength, modulus of elasticity and ductility of polyester, vinyl ester and epoxy resin based PC was investigated. It was found that polymer concrete mortar can achieve compressive strengths in the range of 90–100 MPa. Tensile strength was 15 MPa for vinyl ester based polymer concrete. The results showed that polymer based filler materials are suitable for
both compression and tensile loading applications (Lokuge and Aravinthan, 2013). The optimum proportions of fly ash for optimum compressive strength was 10%. It was also concluded that the addition of fly ash as a filler material resulted in a reduction in the amount of resin, and an increment in the compressive strengths for PC with all the three types of resins. Ductility improved with decreasing fly ash content for all the mixes of PC concrete. Therefore confinement methods need to be addressed properly if PC with fly ash is to be used in structural applications. Modulus of elasticity increased with increasing fly ash content for all the mixes of PC concrete. Split tensile strength and flexural strength exhibited a decreasing trend with an increase in fly ash content for all the mixes.

2.6.1 Maturity and long-term properties of polymer concrete

Long term properties of polymer concrete such as creep have a great effect on the performance of the PC material. Understanding the creep behaviour and when the creep stop or going to the minimum determine the time line for the mounting process of the precision machine parts to commence on the PC base. Measuring the creep under various loads will provide a figure of the suitable load to obtain the minimum creep, literature suggested several measures under different kinds of loads for PC containing various resin. There is a relationship between the maturity and the creep. Increasing the maturity reduce the creep. Cirrode investigated the creep under a compressive load of 19.6 MPa, creep did not stabilised for 2.5 years with a strain of 1800 ×10^-6 (Brocard and Cirrode 1967) for a PC with epoxy binder. Two thirds of the stretch was reached in two months. The nature of the creep strain was to increase in a non-linear fashion with the creep stress.
Tolbert and Hackt investigated the viscoelastic nature of polymer concrete, using an epichlorohydrin/bisphenol A-type epoxy as a thermosetting binder. The composition of the aggregates was 60% river gravel, 30% sand and 10% Portland cement Type II. Compression samples were tested for the linearity of viscoelastic behaviour (Tolbert and Hackt, 1979). The effect of mass size on creep for the determination of the specific creep compliance and the associated elastic modulus was researched. The creep compliance was determined by the least squares curve fitting of the experimental creep data. Collocation a numerical Laplace transform inversion routine was utilized in developing the equation for the relaxation modulus. It was found from the results of the superposition and creep tests that the PC behaved in a viscoelastic fashion linearly at the lower stress regions (Tolbert and Hackt, 1979). Further testing was essential to characterise the degree of linearity throughout the material’s useable stress region. It was noted that the behaviour of polymer concrete is similar to Portland cement. The creep rate of epoxy PC is slightly higher and the values of the relaxation modulus which were similar to Portland cement at the initial stage (Tolbert and Hackt, 1979).

Howdyshell investigated the creep characteristic of polymer concrete. The resin binder was UPE, and methyl ethyl ketone peroxide (MEKP) was the initiator (Howdyshell, 1972). Stress-strain was measured and constructed using both mechanical and electrical methods. The average compression strength was 88.94 MPa. It was observed that the stress-strain relationship started to be non-linear at 50% of the ultimate load. The average modulus of elasticity was 23.09 GPa. Creep was experimented with three stress levels: 23%, 44% and 66% of compressive strength for 1000 hours. Creep samples suffered from premature failure at a stress strength ratio of 0.48 preceded by a sudden increase in creep rate, except for the
23% of compression strength samples that withheld for 1000 hours (Howdyshell, 1972). Ultimate creep strain to elastic strain was 1.23. Creep recovery was about 50% of creep strain and the compressive strength did not drop after 1000 hours for 23% creep load. It was observed that the creep deformation is sensitive to temperature. In another study a compressive creep test on polymer concrete using unsaturated polyester resin as a binder was conducted (Ohama, 1974). The following equation was developed as an outcome of the experimental data expressed below:

\[ e_c = \frac{t}{A + Bt} \] 

(2.1)

Where \( e_c \) is the creep strain A and B are arbitrary constants. A low stress to strength ratio was used for the experimental set up, and the highest creep strain was 0.18.

In another study on creep in polymer concrete. The creep caused by compressive strength on epoxy based PC was investigated (Broniewski and Jamrozy, 1975). A model was developed that describes the creep as shown in equation 2.2.

\[ e_t = e_0 \left( \frac{t}{b} \right) \] 

(2.2)

where \( b \) is arbitrary constants, \( e_t \) time dependent strain and \( e_0 \) the initial strain. Equation 2.2 can be used in a PC system with or without fibre reinforcement. An attempt was made to describe the creep behaviour in UPE as well as epoxy based polymer concrete. A triple superposition scheme was undertaken to develop a constitutive equation for the forecast of long term creep in PCs (Dharmarajan,
1987). The investigation was done on the influence of stress, temperature and resin content on the creep responses of the PC, minimising the data onto the preferred reference state. By successfully minimising the data, it was made possible to elaborate the creep compliance of PC systems as a product of different separate features of time \( (t) \), stress \( (S) \), temperature \( (T) \) and resin volume fraction \( (V) \), such as:

\[
J(t,T,S,V) = J_s \exp \left( -\frac{H}{RT} + K_s + tK_v \right) 
\]

Another serious attempt to predict the creep of polymer concrete was made. The principle of time temperature equivalence was used to predict the long term creep of polymer concrete (Khristova and Aniskevich, 1995). In another study, the physical aging of the polymer binder was seen to influence the creep of polymer concrete. To predict the long-term creep accounting for the aging process, the result of the experimental study of UPE resin-based concrete and its structural components (an unfilled resin and a resin filled with diabasic flour), a function of the time–temperature–aging time reduction was applied. It was found that the changes in the creep compliance of the material followed according to the principle of the time–aging equivalence, with the reduction function dependant on the aging temperature (Khristova and Aniskevich, 1995).

Chen and Liu conducted a study on different parameter that effect the creep of PC which is thermo-moisture creep of polymer concrete under compressive load utilizing time-temperature-moisture analogy (superposition) for a short term (10 hours) (Chen and Liu, 2005). The temperature and moisture contents were constants during the test. A model for the creep behaviour of PC was created
which has the ability of to predict the creep by knowing the temperature and moisture environment.

In another study by Tolbert and Hacket, a group of parameters were investigated in an effort to understand how a variation of a specific parameter could affect the compressive strength (Tolbert and Hacket, 1976). Parameters included were: polymer loading, catalyst, exothermic reaction, aggregate type, graduation and moisture content, curing age, aggregate additives and Portland cement. Epichlorohydrin bisphenol A-type epoxy resin was used as a thermosetting binder. It was found that the type of aggregate affects the compressive strength. The optimum amount of diethylenetriamine catalyst for maximum compressive strength was near 10%. Levels of catalyst between 8 to 12 % provided acceptable results. By reducing the amount of catalyst, the exothermic temperature of the mixture could be reduced. The use of moist aggregate reduced the compressive strength substantially, my research agreed with the moisture effect on compressive strength. The use of Portland cement as an additive could negate the majority of this reduction (moisture effect) when added in the proper quantity. The curing period beyond 7 days affected the compressive strength, although the increase in curing period had a significant effect on compressive strength.

While it is interesting to explore the literature of long term properties of polymer concrete and the key parameters that were studied, it is also essential to consider maturity and how it effects on the mechanical strength of PC. In a study about maturity, the strength development of polymer concrete through different maturing environments was investigated (Ohama and Demura, 1982). Polymer concrete samples were prepared and cured in various conditions. The compressive strength was then measured for the cured specimens. It was found out that the
optimum maturation time before an elevated maturing temperature for the resin concrete was about 10 hours. A water cure was found to be applicable and was damage-free for polymer concrete using unsaturated polyester as binder. The maturity method of PC using UPE as a mortar and how to implement the gaining of high compressive strength was investigated (Lee et al., 1997). The key controls of the maturity study were identified, namely catalyst, accelerator and temperature, as a function of curing time and compressive strength. Polymer concrete samples were prepared and cured at different temperatures with a variety of accelerators and catalyst contents, and then the compressive strength was measured for each case. Maturing temperature-compressive strength relationships were built and the datum temperature was estimated. It was concluded that the datum temperature for maturity equations for polymer concrete with different combined catalyst and accelerator contents could be estimated using temperature-compressive strength relationships. The compressive strength of polymer concrete could be forecast by using the following equation:

\[
\sigma_c = A + B[1 - \exp(-c \log M_p)]
\]

(2.4)

where \(\sigma_c\) is the compressive strength of polymer concrete that is measured by MPa. \(M_p\) is the maturity of polymer concrete. A, B and C are constants. Maturity of polymer concrete is represented by the following equation:

\[
M_p = (T - T_0)\sqrt{\Delta t}
\]

(2.5)
Where $T$ is the maturing temperature ($^\circ$C) of polymer concrete. $(T_a)$ is the datum temperature ($^\circ$C) below which polymer concrete does not gain any compressive strength (Ohama and Demura, 1982).

Maksimov, R. D. et al. (1999) studied the creep of PC under compression load. The formula of the concrete was established using an experimental-calculation approach, and by using this method a highly compacted filler composition was obtained (Maksimov et al., 1999). It was found that the compressive strength was high under prolonged compression loads. The polymer-concrete also exhibited noticeable creep behaviour with a linear relation between the creep strains and stresses. After the action with half the ultimate load of over 3000 h, the total strains exceed the instantaneous ones by 2.0 to 2.2 times. An accumulation of irreversible strains was also observed, although their contribution to the total strain was small. It was concluded that the stress-strain relation can be represented by the equation of linear hereditary creep theory (Maksimov et al., 1999).

2.7 Polymer concrete for manufacturing the bases of precision tool machines

McKeown and Morgan (1979) wrote the first engineering article describing the benefits of using PC containing granite as aggregate and epoxy as a thermosetting binder to produce precast components for items such as the bases for precision tool machines. The comparison of PC, cast iron and granite was detailed in terms of mechanical properties such as high damping factor, dimensional stability and reasonable rigidity. Another benefit of PC is the manufacturing process compared to cast iron. It was found that cast iron is not easy to handle and is costly, and needs further machining. PC pre-casting has ease of manufacture, feasibility, and
the ability to embed plastic pipes. PC also costs less than cast iron (McKeown and Morgan, 1979).

Morgan and McKeon (1979) compared mechanical properties of materials used to manufacture precision tool machine bases (Morgan and McKeon, 1979). Several materials were involved in this comparison, including cast iron, hydrolytic concrete, mild steel, granite and PC. The comparison of the materials was in terms of their properties, including the modulus of elasticity, specific stiffness, damping, long-term dimensional stability, coolant resistance, wear rate, frictional properties, thermal conductivity and lead time for manufacture. It was concluded that each material compared had limitations. PC containing epoxy as a resin binder seems to have most advantages compared to most of the reviewed materials for a machine tool structure. Other advantages of PC are that it can be cast to size quickly and precisely, it is low-cost, has a short manufacturing lead-time, high damping ratio, and high stiffness. It is unaffected by coolants and is stable dimensionally.

Kim et al. (1995) studied the properties of PC for a machine tool base using epoxy (IPCO 410) as a mortar. Numerous experiments were conducted to obtain the best properties of PC for the application. The modulus, compressive strength, flexural strength, CTE, specific heat, thermal conductivity, and damping factor were measured by varying the compaction ratios, sizes and ingredients to assess the effect of the processing parameters on PC properties. It was found that the optimal compaction of PC was obtained when the pebble weight fraction was 55.5%. The Young’s modulus and compressive strength increased, as the pebble weight fraction increase for overall aggregate weight was constant in PC composite systems. The Young’s modulus, compressive strength and flexural strength increased as the resin content increased, as well as the CTE. When the resin weight
fraction was 7.5%, the CTE of PC was the same as that of cast iron (Kim et al., 1995).

Orak (1999) investigated the usability of polymer concrete in the manufacture of machine tool beds. The research was involved in damping characteristic of PC. PC samples were prepared with equal amount of UPE resin and different quartz material ratios were used in order to investigate (Orak and Karademir, 1998) changes in the damping characteristic with structure. Damping experiments were conducted using PC and cast iron samples for compression purposes. Critical damping ratios were calculated with the free vibration method. It was observed that the critical damping ratio of polymer concrete was approximately 4-7 times higher than that of cast iron.

Other research in which a hybrid PC base for high-speed CNC milling was designed and manufactured was conducted by (Suh and Lee, 2008b). The base was composed of PC and welded steel structure faces. The dynamic characteristics of the resin (unsaturated polyester) and the main aggregate (granite) were measured by impulse dynamic tests according to ASTM C215-91. The damping factor of the base was validated using ANSYS 6.0 CAE software. The hybrid base damping factor was compared with steel and cast iron damping factors. The hybrid PC machine base exhibited superior damping characteristics (n = 2.93–5.69%), which enhanced the precision of the CNC milling machine.

In another study with the same focus (Bruni et al., 2008), the effect of a PC base for a CNC turning machine on dimensional accuracy and tool wear was
investigated using 39NiCrMo3 alloy steel in a hard turning operation and the results were compared with a cast iron base for a CNC turning machine. In this research, two kinds of cutting tools were used. They were ceramic and PCBN, with lubricant and without. Figure 2.2.7 shows the effect of the machine base material on tool wear and surface roughness. The general trends obtained under the same experimental conditions using the cast iron and PC beds are very similar. However, it can be observed that the machine tool equipped with the PC base, in respect to the insert material and the lubrication-cooling technique used, obtained a better surface finish and lower tool flank wear than those given by the cast iron base.

![Figure 2.2.7](image)

**Figure 2.2.7** (a) Flank wear versus cutting time, (b) surface roughness versus cutting time obtained using polymer concrete and cast iron beds under wet and dry turning conditions (PCBN inserts).

Figure 2.2.8 shows the comparison between the two bases used, in terms of acceleration time history and the spectrum measured during free vibrations after an excitation was applied using an impulse hammer. It demonstrates that the PC
base is characterized by vibrations with lower amplitude and resonance peaks than those measured on the cast iron base (Bruni et al., 2008).

![Comparison between cast iron and polymer concrete base in terms of (a) acceleration time history and (b) spectrum measured during free vibrations.](image)

Figure 2.2.8 Comparison between cast iron and polymer concrete base in terms of (a) acceleration time history and (b) spectrum measured during free vibrations.

It was concluded from these results that the surface finish and turning performed on the machine tool equipped with the PC base provided lower flank wear and higher surface finish values than those given by the same operations carried out on the turning centre equipped with the cast iron or steel bases (Bruni et al., 2008).

Bai et al. (2009) investigated the influence of glass fibre on the mechanical properties of PC used as a base for precision tool machines. The most effective property in PC is the damping ratio. Damping tests were performed for different PC samples containing different levels of glass fibre, and different amounts of epoxy resin and granite. Results of the tests showed that the granite volume fraction had more influence on the damping ratio than the epoxy dosage and glass
fibre length, while the amount of resin and the glass fibre dosage had comparatively less influence (Bai et al., 2009).

Ding (2010) conducted another study on bases for CNC machine tools composed of epoxy concrete structure faces and steel fibre, with a cement concrete core (Ding, 2010). This combination of materials satisfied the required properties of high stiffness and high vibration damping for the machine base, and its low cost was advantageous. Figure 2.10 illustrates a cross-section of the machine base.

![Cross-section of the CNC machine bed](image)

**Figure 2.2.9 Cross-section of the CNC machine bed (Ding, 2010).**
2.8 Conclusion

In conclusion, Flandro established a progressive principal for PC research more than 50 years ago, which then PC research continued in various directions depending on the application and research approach. This literature review was structured to include discussion of the different types of thermosetting resin binders, the use of thermosetting resins in PC, and the applications of PC in the manufacture of bases for a precision tool machine. All the directions of PC research since Flandro were covered in this chapter. Each direction in PC research focuses on different aspects, depending on the application, the research approach and previous research. The PC aspects were reviewed in regard to the effect of polymeric material, such as the damming ratio, mechanical properties and thermal properties. In respect to the PC as a composite, various aspects were reviewed, such as fillers, polymeric matrix, curing behaviour, creep behaviour, principal mechanical properties and thermal properties. Recently, a major focus of PC research has been the utilization of PET bottle waste as a filler or resin in the manufacture of PC, being an innovative and environmental approach to the utilization of the waste with many useful applications. The literature review identified numerous gaps. Some of those gaps were related to issues in the manufacturing of PC bases for precision tool machinery, such as:

1. Resin optimization for the mechanical and rheological properties in accordance with the manufacturing process of PC and the final structural functionality of precision tool machine bases. This thesis is filling this gap as described in Chapter 4.

2. Investigation of the allowable moisture content in fillers, based on the influence of water on the mechanical, thermal and rheological properties of the polymeric binder and the PC composite system.
The investigation filling this gap as described in Chapter 7 and the amount of allowable moisture nominated.

3. Investigation of the effect of resin and filler volume fractions on the CTE, damping characteristics and mechanical strength of the PC composite system. This thesis filling this gap as described in Chapter 5.

4. Investigation into the effect of moulding technology, including the optimisation of mixing, maximum compaction and vibrating time, based on the rheological properties of the resin bidder, morphological properties of the filler and resulting mechanical properties. This gap is covered in Chapter 6, where the optimum vibration frequency and time are identified.

5. Identification of the amount of DMA according to the temperature-time dependant rheological properties of polymeric binder and how they affect the mechanical properties of the resin and PC composite. This gap is covered in Chapter 6, which nominates the DMA amounts according to the temperature and rheological properties of the matrix.

6. Nomination of the maximum allowable moulding period based on curing studies and the temperature-time. This gap is covered in Chapter 6.

7. Identification of a maturing method, compatible with the required mechanical strength of the base according to the optimization
criteria. This gap is investigated in Chapter 8 and the maturing method is identified based on flexural strength.

8. Identification of the relationship of the PC developed flexural strength with the maturing time and maturing temperature. This gap is covered in Chapter 8, and the relationship identified for developed flexural strength with the maturing time and maturing temperature.

There are other gaps not related to the research area of PC used in the manufacture of bases for precision machines, such as:

1. The effect of the virgin material of MMA monomer on the mechanical properties and curing behaviour of UPE obtained from the depolymerisation of PET bottle waste.

2. The effect of DMA amounts on the curing rate and mechanical properties of UPE obtained by the depolymerisation from HDPE bottles.

3. The relationship between the developed strength on PC contained UPE obtained from PET bottle waste and the temperature with the time.

4. The comparison of UPE virgin material and the UPE obtained from PET bottle waste in terms of thermal properties, such as CTE and thermal conductivity.

5. The effects of gamma radiation on the thermo-mechanical properties of PC containing a UPE as a polymeric binder obtained from PET bottles.

6. The effect of thermal stress and shrinkage induced by the thermal maturing on PC mechanical properties of PC containing UPE obtained from PET bottles.
7. The effect of initiators on the rheological and thermo-mechanical properties of UPE obtained from UPE bottles.

8. The suitability of the PC containing UPE as a resin binder obtained from PET bottle waste in the manufacture of a PC base of for a precision tool machine and how it can be accommodated.

9. The use of surfactants as a chemical binder between the aggregates and the matrix to improve the mechanical properties of PC in UPE of a virgin material and the UPE obtained from PET bottles.
Chapter 3

Materials and Methods

3.1 Polymeric matrix

The resin used in this research is a thermosetting material combining two commonly used constituents, commercial unsaturated polyester (UPE) and a vinyl based monomer, methyl methacrylate (MMA). The resin is formed via the radical copolymerization of the monomer (MMA) and the low molecular weight unsaturated polyester (UPE) viscose liquid when initiator (methyl ethyl kenton peroxide (MEKP)), an accelerator (dimethyl aniline (DMA)) and a promoter, cobalt octoate, are added to bring about the curing reaction. This process produces a cross-linked three-dimensional network resin. This resin is used as a binder for aggregates in PC composite systems.

3.1.1 Unsaturated polyester (UP)

UPE resin is available referred to commercially as a combination of unsaturated polyester with styrene. The resin offers ease of handling, and casting and moulding operations with little or no pressure (Zaske and Goodman, 1998). The
commercial general purpose UPE (AROPOL) is manufactured by the Mitsubishi Chemical Company in Japan and imported by Hustman Chemical Company Australia Pty. Ltd. The appearance can be a clear or cloudy, viscous liquid with a sweet or sharp aromatic odour. Table 3.3.1 provides information provided by the manufacturer. The molecular chemical structure is shown in Figure 3.1:

![Chemical structure of UPE.](image)

Table 3.3.1 UPE properties supplied by the manufacturer.

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapour pressure</td>
<td>Styrene: 4.5 mmHg @ 20 °C</td>
</tr>
<tr>
<td>Water solubility</td>
<td>Immiscible</td>
</tr>
<tr>
<td>Vapour density</td>
<td>Styrene: 3.6</td>
</tr>
<tr>
<td>Solubility in organic solvent</td>
<td>Miscible with acetone, glycol ethers, toluene</td>
</tr>
<tr>
<td>Evaporation rate</td>
<td>Styrene: 0.5</td>
</tr>
<tr>
<td>Percentage of Volatile</td>
<td>30 – 67% by volume</td>
</tr>
</tbody>
</table>

3.1.2 Styrene

Styrene is commonly used as a monomer with UPE. It is a low-cost monomer and can produce low-viscosity resins that can polymerise with UPE at either room
temperature or at a high temperature. The styrene used in this study was produced by Nupol Composites, a division of Nuplex Industries (Aust) Pty Ltd NSW, Australia. The specifications, as supplied by the manufacturer, are shown in Table 3.2. Styrene monomer has a composition of 99-100% of styrene and 10-15 ppm of tertiary butyl catechol (TBS) which is a polymerisation and oxidation inhibitor.

Table 3.2 Styrene specifications provided by the manufacturer.

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapour density (air=1)</td>
<td>3.6 (air=1)</td>
</tr>
<tr>
<td>Evaporation rate</td>
<td>0.49 (n-butyl acetate = 1)</td>
</tr>
<tr>
<td>Odour threshold</td>
<td>Approx. 0.1 ppm</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>104.14</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.902 @ 25°C</td>
</tr>
<tr>
<td>Auto-ignition (°C)</td>
<td>281</td>
</tr>
<tr>
<td>Water solubility</td>
<td>Insoluble 0.300 g/L @ 20 °C</td>
</tr>
<tr>
<td>Viscosity (mPa.s)</td>
<td>0.763 @ 20 °C</td>
</tr>
<tr>
<td>Vapour pressure (kPa)</td>
<td>0.6 kPa @ 20 °C</td>
</tr>
</tbody>
</table>

3.1.3 Methyl methacrylate (MMA)

This organic compound is a monomer with low viscosity. It is colourless and has a sharp fruity odour. It contains 0.25% inhibitor of hydroquinone to avoid
premature polymerisation, and is supplied by Degussa Australia Pty Ltd. Table 3.3 illustrates some of its properties, as provided by the supplier.

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.94</td>
</tr>
<tr>
<td>Flammability limits (%)</td>
<td>2.1-12.5</td>
</tr>
<tr>
<td>Water solubility (g/L)</td>
<td>15.9</td>
</tr>
<tr>
<td>Viscosity (mPa.s)</td>
<td>0.63</td>
</tr>
<tr>
<td>Vapour pressure (Pa)</td>
<td>38.7</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>100.3</td>
</tr>
</tbody>
</table>

3.1.4 Methyl Ethyl Ketone Peroxide (MEKP)

Organic peroxide initiators are the source of free radicals in a variety of plastic resins and elastomers. They are used in plastic processing for the polymerisation of thermoset resins such as the curing of unsaturated polyester, cross linking of polyethylene and various elastomers. There are other kinds of initiators, such as cyclohexanone peroxide and TMPTMA. The peroxide group (—O—O—) that is contained in all organic peroxides is highly unstable. When the bond is broken between two oxygen molecules, the peroxide decomposes and two free radicals are formed. The general formula for these compounds is R1—O—O—R2, where R1 and R2 either symbolize organic radicals or an organic radical and hydrogen atom. MEKP is the main product of the organic ketone peroxides. These types of
Peroxides are mixtures of peroxides and hydro-peroxides that are commonly used for room-temperature polyester curing (Kattas et al., 2004). MEKP is a product of FGI, a division of Nuplex Industries Australia Pty Ltd. Table 3.4 contains information provided by the MEKP supplier.

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.15</td>
</tr>
<tr>
<td>Auto-ignition (°C)</td>
<td>281</td>
</tr>
<tr>
<td>Water Solubility (%)</td>
<td>1</td>
</tr>
<tr>
<td>Viscosity (mPa.s)</td>
<td>0.63</td>
</tr>
<tr>
<td>Vapour Pressure (kPa)</td>
<td>50 @ 50°C</td>
</tr>
<tr>
<td>Appearance</td>
<td>Colourless liquid</td>
</tr>
</tbody>
</table>

### 3.1.5 Promoter

A promoter is a compound that greatly increases the activity of a given initiator. The promoter helps in the decomposition of the initiator, delivering radicals at low temperatures. Promoters facilitate curing because the initiator alone does not decompose at a sufficient rate (Fink, 2005). The promoter used in this study was cobalt octoate, a product of Alfa Aesar Pty Ltd from USA. Cobalt octoate is a metallic salt of synthetic carboxylic acid containing 1-12% of cobalt metal and a mineral spirit as the diluent. Some typical properties of cobalt octoate specifications, provided by the supplier, are shown in Table 3.5.
Table 3.5 Cobalt octoate supplier specifications in different concentrations.

<table>
<thead>
<tr>
<th>Cobalt octoate concentration</th>
<th>(12%)</th>
<th>(10%)</th>
<th>(6%)</th>
<th>(3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal content</td>
<td>12</td>
<td>10</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Non-volatile matter</td>
<td>69</td>
<td>60</td>
<td>33</td>
<td>19</td>
</tr>
<tr>
<td>Specific gravity @ 30°C</td>
<td>1.02</td>
<td>1.97</td>
<td>0.87</td>
<td>0.83</td>
</tr>
</tbody>
</table>

3.1.6 Accelerator

A chemical compound is used to increase the reaction or curing of thermosetting materials. Note that the term “accelerator” is often used interchangeably with “promoter”. An accelerator is often used with a catalyst, hardener or curing agent (Kattas et al., 2004). The accelerator used in this study was dimethyl aniline (DMA), a product of Alfa Aesar Pty Ltd, USA. It is a colourless gas with an ammonia-like smell. Some properties of DMA, as provided by the supplier, are shown in Table 3.6.
Table 3.6 DMA Supplier specifications obtained from the supplier.

<table>
<thead>
<tr>
<th>Property</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (g/mol)</td>
<td>100.1</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.049</td>
</tr>
<tr>
<td>Viscosity (mPa*s)</td>
<td>0.66</td>
</tr>
<tr>
<td>Solubility in water (%)</td>
<td>1.15 @ 20 °C</td>
</tr>
<tr>
<td>Boiling point (C°)</td>
<td>100.5</td>
</tr>
<tr>
<td>Melting point (C°)</td>
<td>-48</td>
</tr>
<tr>
<td>Shrinkage on polymerisation (%)</td>
<td>21</td>
</tr>
<tr>
<td>Vapour pressure (mbar)</td>
<td>37 @ 20 °C</td>
</tr>
</tbody>
</table>

3.2 Specifications of filler composition of polymer concrete

The aggregates used in PC are basalt, river gravel, spodumene, sand, chalk and fly ash in different combinations. Basalt, river gravel, sand and chalk were used as filler aggregates in the present study.

3.2.1 Basalt

The basalt that used as coarse aggregate in this research was basalt 7 mm from Roca Pty Ltd. The specifications of the basalt are shown in Table 3.7. The basalt
was selected as coarse aggregates since basalt provide a high rigidity and low CTE. The ecological source of basalt was Walsh Ballarat quarries.

<table>
<thead>
<tr>
<th>Property</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>3.00</td>
</tr>
<tr>
<td>Chemical stability</td>
<td>Stable</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Immiscible</td>
</tr>
<tr>
<td>Odour</td>
<td>Odourless</td>
</tr>
</tbody>
</table>

### 3.2.2 Gravel

The gravel used as course aggregate in preparing PC samples was 7 mm gravel from Roca Pty Ltd. The specifications of the gravel are shown in Table 3.8. The gravel was selected for a comparison resin with the basalt. The ecological source of gravel was Kingston quarries in Melbourne.
Table 3.8 Specifications of gravel delivered by the supplier.

<table>
<thead>
<tr>
<th>Property</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>2.80</td>
</tr>
<tr>
<td>Chemical stability</td>
<td>Stable</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>immiscible</td>
</tr>
<tr>
<td>Odour</td>
<td>Odourless</td>
</tr>
</tbody>
</table>

3.2.3 Sand

The sand used in the present study in the preparation of the PC samples was a middle-sized aggregate supplied by Roca Pty Ltd. The basalt was selected because of its availability and high compaction. The ecological source of sand was Essendon quarries in Melbourne. The specifications of the sand are shown in the following table:

Table 3.9 Sand specifications obtained from the supplier.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>2.6</td>
</tr>
<tr>
<td>Chemical stability</td>
<td>Stable</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Immiscible</td>
</tr>
<tr>
<td>Odour</td>
<td>Odourless</td>
</tr>
</tbody>
</table>
3.2.4 Spodumene

Spodumene is a lithium aluminium silicate. It is a non-toxic and inert substance, unlike lithium, which is a reactive substance. Spodumene is a source of lithium for applications such as batteries. The spodumene was selected because of it is very low CTE and high texture. The spodumene was supplied by Talison Minerals, Western Australia Pty Ltd. The chemical contents of spodumene provided by the supplier are shown in Table 3.10.

Table 3.10 chemical contents of spodumene obtained from the supplier.

<table>
<thead>
<tr>
<th>Chemical content</th>
<th>Volume fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$O</td>
<td>5.0</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.1</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>18.5</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>75.0</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.25</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.35</td>
</tr>
</tbody>
</table>

3.2.5 Fly ash

Fly ash is a fine grey powder consisting mainly of spherical glassy particles that are produced as a by-product in coal fired power stations. The fly ash was
supplied by Cement Australia Pty Ltd. The geological source is Bayswater power plant. The fly ash specifications are shown in Table 3.11.

Table 3.11 Fly ash specifications obtained from the supplier.

<table>
<thead>
<tr>
<th>Property</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.4</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1400</td>
</tr>
<tr>
<td>PH</td>
<td>Basic (11.9)</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>1.3 mg/100g</td>
</tr>
<tr>
<td>Odour</td>
<td>Odourless</td>
</tr>
</tbody>
</table>

3.2.6 Chalk

Chalk is a porous powder from limestone composed of mineral calcite (CaCo3). The chalk used in the study was supplied by Omya Australia Pty Ltd. The specifications of the chalk are shown in Table 3.12
3.3 Methods of measuring properties of fillers

Different properties were measured for each aggregate, including particle size distribution, bulk density, true density, Brunauer, Emmett, and Teller (BET) surface area and morphological properties using scanning electron microscopy (SEM). The methods of testing are explained in the following sections:

3.3.1 Sieve analysis

Particle size distributions were obtained for course and middle-sized aggregates such as basalt, river gravel, sand and spodumene using sieve analysis with different sieve sizes, depending on aggregate particle size distributions. The procedure starts with a nest of sieves that is prepared by stacking the test sieves one on top of another. The largest opening is at the top, followed by sieves with progressively smaller openings and a catch pan at the bottom. A sample of 400g
dry aggregate is poured onto the top sieve to cover the nest which is then shaken mechanically for 10 minutes until each particle has dropped to a sieve with openings too small to pass, thus retaining the particle. The accumulative weight of all material larger than each sieve size is determined and divided by the total sample weight to obtain the percentage retained for that sieve size. This value is subtracted from 100% to obtain the percentage passing that sieve size. The results are displayed after plotting the percentage passing through the sieve opening size and connecting the plotted points with a smooth curve.

3.3.2 Determination of the particle size distribution using laser scattering

The particle size distributions of micro-size fillers such as chalk and fly ash were obtained using a Malvern Mastersizer X, manufactured by Malvern Instruments Ltd. UK. This equipment was implemented because the filler particle size cannot be detected using conventional sieves, and accurate results were needed to enhance the research outcomes. This method operates on the observation of patterns of light scattered at various angles, which is one way of measuring particle size distributions (Frock, 1987). The low angle scattering method can be applied to particles with large dimensions compared to the wavelength producing the scatter. The method relies on the fact that the diffraction angle is inversely proportional to the particle size. The optical configuration is shown schematically in Figure 3.2. The instrument is equipped with a low power helium-neon laser that measures particles with a maximum size of 600 μm with an accuracy of 2% on volume median diameter. The results of particle size distribution measurements at a wavelength of 0.63 μm, are used to form a collimated beam of light. Particles are introduced to this beam by the sample presentation modules and scatter the laser
light. The light scattered by the particles and the unchartered remainder is analysed by the special semiconductor detector in the form of a series of concentric annular sectors. Figure 3.2 shows a schematic diagram of the laser scattering process. The results are converted into an electronic signal sent to the computer for analysis by special software provided with the instruments. Figure 3.3 shows the computer results that can be converted into an Excel file using interface software.

Figure 3.2 Schematic configuration is of Malvern Mastersizer X.
3.3.3 Bulk density

Bulk density was measured using a measuring cylinder in a simple procedure. The sample was weighed then poured into a measuring cylinder then compacted into the measuring cylinder. The volume of the sample was obtained using the measuring cylinder and the mass of the sample was known. The density was calculated by dividing the mass over the volume.
3.3.4 True density

The density of the aggregates was measured using a pycnometer (density bottle). The dry bottle, aggregate sample and bottle with sample and acetone were weighed and the sample weight, volume and density were calculated accordingly.

3.3.5 BET (Brunauer, Emmett, and Teller) surface area

The BET specific surface areas and porosity were determined using nitrogen sorption measurements that were performed using a Micromeritics ASAP 2000 (USA). Surface area and porosimetry were determined by nitrogen gas adsorption/desorption. In a typical test, a 100-150 mg sample was degassed at fixed temperatures under high vacuum for at least 22 h, prior to measuring the isotherms at liquid nitrogen temperature (77°K). The same samples were degassed at gradually increasing temperatures up to 250°C and the N₂ adsorption isotherms were measured after each step of degassing using an 89-point pressure table with 15 s equilibration intervals. The surface areas were determined using the BET method, and the average pore diameter and pore size distribution were evaluated using the Barret, Joyner and Halenda (BJH) theory applied to the desorption branch.

3.3.6 Method of measuring aggregate moisture content

The moisture content of the aggregates has a great effect on the mechanical properties and curing behaviour of a PC composite system. Prior to mixing the aggregates with resin, a moisture test should be performed to obtain an indication of the moisture levels in the system. The level of moisture in the aggregates is preferably
at zero or as close as possible. The device used for measuring the moisture content of aggregate was an MD 150 from Sartorius, Germany. This is a specialized measuring instrument for this application. The MD 150’s working principle is that thermo-gravity determines the loss of mass that occurs when substances are heated. In this process, the sample is weighed before and after being heated and the difference between the two weights is determined, which is the moisture content. The heating element in the MD 150 is infrared radiation, which has high heat penetration. The procedure takes up to 30 – 40 minutes, with a gentle heating temperature of 150 °C.

3.4 Methods of testing polymeric matrix

The polymeric matrix was tested for different properties, such as flexural strength, tensile strength, modulus of elasticity, elongation, hardness, the damping factor and the CTE. Furthermore, the resin was subjected to numerous analyses to capture a potential explanation for the resin behaviour or parametric effect. Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), rheology analysis and scanning electron microscopy (SEM) were used.

3.4.1 Methods of testing mechanical and thermal properties for polymeric matrix

Different mechanical properties of the polymeric matrix were tested, including tensile strength, flexural strength, shore D hardness, damping factor and CTE. In the next sections, each method of testing mechanical properties is described in detail.
3.4.1.1 Methods of testing tensile and flexural strength

Flexural strength and tensile strength were tested using a Zwick universal testing machine (Zwick Z010, Germany), as shown in Figure 3.4. Resin samples were prepared using a high density polyethylene (HDPE) mould with the following dimensions: 50 mm long × 10 mm wide × 2.5 mm thick.

![Zwick universal testing machine](image)

**Figure 3.4 Zwick universal testing machine.**

For tensile testing, a sample is inserted in both jaws of the universal testing machine at the centre of the jaws in a vertical orientation. The cross sectional dimensions of the sample are measured using a dial calliper and the dimensions are then entered into the testXpertII software available on the computer connected to the universal machine. The cross-head speed is 25 mm/min, since once the set-up is accomplished, initiating the test can be either by the mechanical start button
on the machine or by the computer software. Once the specimen has failed, the stress-elongation curve can be obtained and the modulus of elasticity for tensile stress derived using testXpertII software. Flexural strength testing was conducted using the same machine by applying a different setting. It was necessary to input the width and thickness of the rectangular sample into the test XpertII software and the span of a simply supported cantilever to obtain the flexural strength and the deflection, as well as the modulus of elasticity for flexural strength.

3.4.1.2 Hardness (Shore D Test Method)

Hardness was tested using a digital Shore D tester 3130/3131 made by Zwick and a check device Zwick 7507. Both combinations were used to measure hardness when using the Shore D Test Method.

The sample was moulded in an HDPE cylindrical mould and machined lightly to the following dimensions: 10 mm diameter and 70 mm length. The time was set for three seconds for measurement by the digital shore tester, and the sample was then placed under the loading hull. The loading hull was pressed until the desired contact pressure was applied, using the actuating lever, the measured value was displayed in the Digital Shore D Tester. Four measurements per sample were performed at four random points.

3.4.1.3 Coefficient of thermal expansion (CTE) for the resin

The CTE was measured using a custom-built device. The device includes a heating chamber (Thumler model TH2700-26, Germany) with two displacement probes attached to a small digital display unit (Sylvac Dsos, Switzerland) and a thermostat connected to a temperature control microprocessor. The resin sample
temperature was monitored using a data acquisition system linked to a computer, as illustrated in Figure 3.5.

Figure 3.5 Measuring device coefficient of thermal expansion (CTE).

Two rods made of Invar (a 36% nickel-iron alloy with the lowest CTE of metals and alloys in the 20 - 230 °C range, \( \alpha = 1.2 \times 10^{-6} \, ^\circ\text{C}^{-1} \)) are used in this set-up. One of the rods is used as a reference and the other one is placed above the PC sample. The expansion of the reference rod and the sample with the second rod is detected by the probes on the top of the heating chamber, which are touching the Invar rods. Figure 3.6 shows the arrangement inside the heating chamber.
The resin sample has a hole at the side wall of the cylinder sample in order to place the thermocouple sensor (SE00 type K thermocouple, Pico Technology, UK), and to monitor and control the temperature inside the sample. The Pico data acquisition system contains a TC-08 thermocouple data logger (Pico Technology, UK) connected to the computer to display the temperature. Due to the low thermal conductivity of PC resin, approximately one hour is required to achieve thermal equilibrium. Thermal expansions at five temperatures: 25, 35, 40, 50 and 60 °C were measured to calculate the CTE of each UPE resin sample using Equation 3.4, which is derived based on the physical principles of CTE as follows:
\[ \Delta L = \alpha_r l_r \Delta T + \alpha_s l_s \Delta T \] ..........(3.1)
\[ \Delta R = \alpha_r l_r \Delta T + \alpha_i l_i \Delta T \] ..........(3.2)
\[ \Delta S = \Delta L - \Delta R \] .................(3.3)
\[ \Delta S = \alpha_r l_r \Delta T + \alpha_s l_s \Delta T - \alpha_r l_r \Delta T - \alpha_i l_i \Delta T \]
\[ \Delta S = \alpha_s l_s \Delta T - \alpha_i l_i \Delta T \]
\[ \alpha_s = \frac{\Delta S + \alpha_i l_i \Delta T}{l_s \Delta T} \]
\[ \alpha_s = \frac{\Delta S}{l_s \Delta T} + \alpha_i \] .................(3.4)

where \( \Delta L \) is the change in length of the Invar rod and the sample within the temperature difference \( \Delta T \), and \( \Delta R \) is the change in length of the reference Invar rod within the same temperature difference \( \Delta T \). \( \Delta S \) is the difference between the readings of the two probes i.e. the difference between \( \Delta L \) and \( \Delta R \). \( l_r \) is the length of the invar rod, which is located in the middle of the resin sample and \( l_s \) is the length of the resin sample. \( l_i \) is the length of the reference rod. Substituting equations 3.1 and 3.2 in to equation 3.3 and using simple algebra simplifications, results in equation 3.4 can be used to calculate the CTE polymer concrete and \( \alpha_s \) is the sample coefficient of thermal expansion.

**3.4.1.4 DMA analysis**

To calculate the resin damping factor, Dynamic Mechanical Analyses (DMA) were conducted, since the damping factor is a dynamic property. DMA is a method where a small deformation is applied to a sample in a cyclic force that leads the materials response to stress, temperature, frequency and other parameters. DMA
applies an oscillatory force at a set frequency to the sample and reports changes in stiffness and damping. DMA data are used to obtain modulus information. A TA Instruments, DMA 2980 USA, was employed to perform a frequency sweep for the dual cantilever test for measuring tan δ (damping factor), storage modulus and loss modulus. The sample size of the resin was the same as that prepared for the mechanical test. A sample is mounted on the clamps and tightened up with screws, using a torque meter to measure the torque while tightening. Each material is tightened to a specific torque according to the instructions provided by TA Instruments. The required torque for PCR was 8 kN/mm. The furnace should be closed and the type of analysis is specified (a frequency sweep, temperature sweep or other available analysis), using the TA Instruments thermal advantage software that controls the device through a computer. Figure 3.7 illustrates the thermal advantage software interface. Analyses that were conducted mainly used the isothermal frequency sweep. Other information which must entered is the deflection, the time for isothermal equilibrium, testing temperature, sample geometry, dimensions, clamp type and sample name.

Figure 3.7 Thermal Advantage software.
The analysis can be run when all the required data are entered. On accomplishing the analysis, the results can be obtained using TA universal software 2000. Figure 3.8 shows the result of a temperature sweep (50-200°C) for a given range of frequencies (1-200 Hz) for UPE resin containing 0.005 DMA accelerator. The analysis illustrates changes in the material damping factor (tan δ) and storage modulus with temperature and time.

![Figure 3.8 TA Universal 200 viewing DAM analysis file.](image)

3.4.2 Rheological analysis

Rheological analysis was conducted in order to understand and analyse the curing behaviour of the polymeric matrix. There are two types, one measuring the viscosity growth due to the cross-linking process through the polymerization, and the other measuring the temperature profile for the resin due to the exothermal reaction that generates heat (exothermal energy). The experimental procedure for
both will be described. Another measure of viscosity growth is the gel time, which is another indication of curing.

### 3.4.2.1 Measurement of viscosity growth during polymerisation

The Brookfield UL (universal left) adapter set was used, which included: a locating channel assembly, chamber tube, collar with thumbwheel, tube end cap and spindle LV-1 with universal coupling. The assembly of a rheological system: All parts of the system are manufactured by Brookfield, USA. The viscosity growth through the polymerisation was measured using the following equipment:

- Brookfield RVDV-II+ Pro programmable viscometer.
- Brookfield UL adapter.
- Brookfield circulating bath with digital controller TC-102.

Viscosity measurement was taken at 25°C for all sample compositions. The Brookfield circulating bath with a digital controller was set at 25°C and the Brookfield UL adapter immersed for a period of 10 minutes to assure thermal equilibrium throughout the chamber tube. In sequence, the Brookfield RVDV-II+ Pro programmable Viscometer was set up to run at a speed of 100 rpm and the entry code for the LV-1 spindle was selected prior to any reading. The Brookfield RVDV-II+ Pro Programmable viscometer ran in stand-alone mode. The locating channel assembly was fixed to the Brookfield viscometer, which was used to assemble the UL adapter with the sample. In order to begin the viscosity measurements, the resin components were mixed according to the composition set. The resin was poured into the chamber tube, followed by insertion of the spindle LV-1 in the chamber and the final assembly of the chamber with the sample, which was connected to the locating channel assembly to run
measurements. The time was recorded with each reading of the viscosity. The flow chart of a viscosity measurement is shown in Figure 3.9.

![Flowchart of viscosity measurement](image)

**Figure 3.9 Flowchart of the procedure for measuring resin viscosity.**

### 3.4.2.2 Method of monitoring resin temperature profile during polymerisation.

The procedure begins by setting the temperature of the Brookfield circulating bath using a digital controller TC-102 for 25°C with a wait time of 10 minutes to obtain thermal equilibrium. The resin is prepared and poured into the high density polyethylene (HDPE) tube, then immersed in the bath and held by a holder, as shown in Figure 3.10. A thermocouple sensor (SE00 type K thermocouple, Pico Technology, UK) is placed in the resin and connected to the Pico data acquisition system containing a TC-08 thermocouple data logger (Pico Technology, UK) and connected to a computer to display to record the temperature profile during the copolymerisation of UPE resin during the copolymerization. Figure 3.10 shows the
experimental arrangement. The resin temperature profile was measured during the polymerization using the following equipment:

- Brookfield circulating bath with digital controller TC-102.
- Tube holder, tube 50 ml.
- Thermocouple sensor (SE00 type K thermocouple, Pico Technology, UK).
- Pico data acquisition system contain TC-08 thermocouple data logger (Pico Technology, UK)(identical to that used in measuring temperature for CTE).
- Computer for data collection system.

![Experimental arrangements for measuring temperature during the curing of the resin.](image-url)
A computer records the temperature and the time using Pico technology software in a pad file that can be converted to an Excel file to plot the temperature versus time.

### 3.4.2.3 Method of measuring gel time

Gel time is the period of time when the resin changes from a liquid to a non-flowing gel. Gel time was determined for the resin according to ASTM D 2471-99 (American Society for Testing and Materials, 2007). A white wooden stick 1 cm in diameter is inserted, then lifted up through a 20 mL resin sample to detect the adherence of the resin to the wooden stick. At the same time, a thermocouple is inserted into the geometric centre of the reacting mixture using the thermocouple data logger PICO system, previously described for the CTE measuring method. At the resin reacting gel stage, when the material no longer adheres to the end of a clean wooden stick, the gel time is recorded.

### 3.4.3 Thermal analysis

Thermal analysis was conducted in order to understand and analyse various aspects of polymeric binder such as conversion rate and mass change rate when the sample under the effect of heat. Those analysis such as:

- Differential scanning calorimetry (DSC)
- Thermogravimetric analysis (TGA)

### 3.4.3.1 Differential Scanning Calorimetry (DSC)

DSC is part of a group of techniques called Thermal analysis (TA), which is based upon the detection of changes in the heat content (enthalpy) or the specific heat of
a sample. As thermal energy is supplied to the sample, enthalpy increases and the
temperature rises by a determined amount, for a given energy input, by the
specific heat of the sample. The specific heat of a material changes slowly with
temperature in a particular physical state, but alters discontinuously at a change of
state. By increasing the sample temperature, the supply of thermal energy may
induce physical or chemical processes in the sample, for example melting or
decomposition, accompanied by a change in enthalpy. Such changes in enthalpy
may be detected by thermal analysis and related to the processes occurring in the
sample. The material, equipment and software used in the DSC measurements
were:

- DSC 2920 Modulated DSC (Figure 3.11-b).
- Thermal Advantage (Version 1.3.0.205), by TA Instruments.
- Precisa 125A Balance (Figure 3.11-a).
- TA Instruments hermetic aluminium pans (Figure 3.11-a).
- TA Instruments T zero press (Figure 3.11-a).
- Eppendorf pipettes.

DSC preparation starts with the weighing of the hermetic aluminium pan, using
the Precisa 125A balance. The resin constituents are then prepared and mixed
constantly and slowly for a few seconds with a mixing paddle. To avoid heat
transfer, the mixing container case is not hand-held. Instead, the mixing container
is placed on an insulated non-conductive surface. The mixture is stirred at room
temperature and a sample of 5-20mg is taken using an Eppendorf pipette and then
sealed hermetically into a hermetic aluminium pan. The hermetically-sealed
sample can either be stored at minus 20°C in order to avoid a reaction or put in the
DSC furnace immediately after mixing and sealing, ready for DSC measurement.
To begin DSC measurement, a sample pan and another empty pan (also
hermetically sealed and used as a reference) are placed into the DCS. Prior to this, the furnace is set up using DSC software (Thermal Advantage software version 1.3.0.205). The DSC furnace is first equilibrated at the isothermal selected temperature, when the sample hermetic pan and the reference pan are placed in the DCS furnace, Figure 3.11(c) and Figure 3.11(d) show the furnace details. Isothermal experiments were established to run at 80 ºC for 180 minutes. Figure 3.12 illustrates the DSC procedure using a flowchart.

Figure 3.11 DSC Analysis: (a) Precisa 125A Balance; TA Instruments Tzero press; and TA Instruments hermetic aluminium pans. (b) Modulated DSC 2920. (c) Modulated DSC 2920 Furnace. (d) Upper view of modulated DSC 2920 Furnace.
3.4.3.2 Thermal Gravimetry Analysis (TGA)

TGA tests weight changes in a material as a function of temperature or time under a controlled environment. Its fundamental uses include measurement of a material's thermal stability and composition. TGA tests were conducted using a Perkin Elmer (USA) TGA7 analyser attached to a TAC controller, gas changer and computer. The samples (2-5 mg) were heated to 700°C at a heating rate of 10°C/min under nitrogen (20 mL/min). A platinum crucible was used as the reference. Ample was scanned at 10 °C/min from 30 °C (close to ambient). At 700 °C automatic gas was switched to air (oxygen present to oxidize and residue to carbon dioxide). At 750 °C the scan stopped, as any residue after air oxidation will not be organic.
3.4.4 Scanning Electron Microscopy (SEM)

The morphology of the samples was studied using SEM. PC resin or PC composite was affixed to aluminium pegs with carbon tape, then sputter-coated with gold for 60 seconds at 0.016 mA (Ar plasma) using an SPI-Module sputter coater (SPI Supplies Division of Structure Probe, Inc.). SEM images were then obtained using a German Zeiss Supra 40 VP electron microscope operating with a high vacuum, as shown in Figure 3.13.

![Figure 3.13 ZEISS Supra 40 VP SEM.](image)

3.4.5 Fourier Transform Infrared Spectroscopy (ATR-FTIR)

ATR-FTIR measurements in attenuated total reflectance mode (Spectrum 100, PerkinElmer) were carried out with a universal diamond ATR top plate accessory in the scanning range 4000 to 550 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\) and with 8 scans for each spectrum.
3.5 Methods of testing polymer concrete composite system

The mechanical properties of PC composite systems were studied and the results are presented in following sections. The method of sample preparation is described prior to all testing methods. Mechanical properties such as compression strength and flexural strength were tested according to Australian standards. CTE were measured using the same techniques as were used for the resin. The structural damping factor was measured for a system containing a PC sample damping factor. This procedure is not a method for measuring the damping factor of PC as a material property it provides an indication of the damping factor for the PC. All the properties that measured is in accordance with the selection criteria of the PC base manufactured for the precision tool machine.

3.5.1 Sample preparation for polymer concrete composite system

Aggregate preparation begins with the preparation of the appropriate amount of each aggregate. In these samples, 60% basalt, 30% sand and 10% of fly ash was used. The overall aggregate volume fraction was 83% and the remainder was resin. Figure 3.14 illustrates all aggregates used in the PC mixes for different compositions.
All the aggregates were kept for three hours inside the vacuum chamber to reduce the moisture content to approximately zero. During this process, the temperature in the vacuum chamber reached 160 °C. When the aggregates cooled down, the moisture content was checked according to the method described in Section 3.3.6. Figure 3.15 shows the vacuum chamber during the drying process of the aggregates.

Figure 3.14 Aggregates used in polymer concrete for different compositions.

Figure 3.15 Drying aggregates using vacuum chamber.
Resin preparation was carried out by mixing the following chemical composition, as shown in Table 3.13, where the resin volume fraction was 17%. Resin volume fraction and aggregate volume fractions varied, depending on the intention of each experiment.

Table 3.13 Resin chemical constituents and volume fraction for each.

<table>
<thead>
<tr>
<th>Chemical constituents</th>
<th>Volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA, (%)</td>
<td>60</td>
</tr>
<tr>
<td>ARAPOLE, (%)</td>
<td>40</td>
</tr>
<tr>
<td>Cobalt peroxide, (%)</td>
<td>0.8</td>
</tr>
<tr>
<td>MEKPT, (%)</td>
<td>2</td>
</tr>
<tr>
<td>DMA, (%)</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Once the resin compounds were mixed with the initiator (MEKP), the PC composite mixing process started by mixing the smallest size aggregates (fly ash or chalk) with the whole amount of resin using a traditional concrete mixer. Once the fly ash had been mixed with the resin until all the fly ash was wetted by the resin, the next size aggregate (sand or spodumene) was added. Mixing continued until the sand and the fly ash were completely wetted. The coarse aggregate was added last. Upon completion, the PC mixture was poured into the mould and, during pouring, the mixture was compacted using a wooden stick. When the pouring of the polymer concrete was finished, the mould was transferred to a vibrating table. G-clamps were used to fix the mould onto the vibrating table for further compaction and particle settling. The frequency was set to 22Hz. The time required for the particles to settle was determined by observation of the resin.
bubbling in the PC composite during the vibration process. The resin started floating after 7-10 minutes or less and the resin bubbling usually appeared to stop after 12-15 minutes. Figure 3.16 shows the mould mounted on the vibrating table. The mixing process for preparing the PC sample was standard sequence of adding the materials. Mixer was a regular concrete mixer, the speed of mixing was 100 RPM and the mix seemed to be non-uniform.

![Figure 3.16 Mould mounted on the vibrating table using G-clamps for sample preparation, (a) compression test mould and (b) flexural tests mould.](image)

Once settled, the sample was transferred to the ventilated curing room to avoid the smell coming from PC as it is an occupational hazard under Health and Safety regulations. The PC samples stayed in the curing room for up to 28 days before being transferred to the testing facility for compressive or flexural tests.
3.5.2 Compressive strength

Compressive tests were carried out according to Australian standards AS 1012-8.2.2000. Cylindrical specimen size was a diameter of 100 mm in diameter × 210 mm high, as shown Figure 3.17.

![Sample for a compressive test (AS 1012.9-1986).](image)

Figure 3.17 Sample for a compressive test (AS 1012.9-1986).

The mould used for making the sample was steel, covered by a releasing agent and gel-coated, as illustrated in Figure 3.18. The purpose of the gel coat was to facilitate the release of the sample.
The testing machine used was a German-built Alpha 3, with two columns, with a crosshead speed of 0.5 mm/min. A ring frame holding three distance sensors was mounted on the sample for lateral displacement, while the machine itself measured the longitudinal displacement. The outcome could be plotted in a stress-strain diagram. Figure 3.19 shows the experimental set up.
3.5.3 Flexural strength

The flexural strength was determined in accordance with Australian standards AS 1012.11-2000 Figure 3.20 and Table 3.14 demonstrate the standard’s test setting for flexural strength. The testing machine is a German built Snitch 60/D, with a universal testing machine load range of 300KN. The crosshead speed during the test was 0.5mm/min, and the calibration remained valid at the time of testing.

Figure 3.20 Test settings for flexural strength according to AS 1012.11-2000.

Table 3.14 Centre-to-centre distance of the supporting and loading roller for 100X100 cross-section samples prepared for flexural strength test.

| Supporting roles \( L_c \) (mm) | 300 +8,-3 |
| Loading roles \( l_s \) (mm)     | \( l = L/3 \) |
The mould was designed using Pro/Engineer software according to the Australian standards, as shown in Figure 3.21 and Figure 3.22. The mould was fully disassembled to overcome all the difficulties that might occur when the sample was fully cured and ready for removal from the mould but a coat of gel was still needed to ease the release of the PC sample from the mould. Figure 3.23 shows the Snitech 60/D during a flexural test.

Figure 3.21 Fully disassembled rectangular mould for preparing a flexural strength sample.
Figure 3.22 Fully disassembled rectangle mould manufactured and ready to be used.

Figure 3.23 Sintech 60/D universal testing machine for conducting a flexural test according to AS 1012.11-2000.
The fracture within the middle third of a specimen’s flexural strength can be calculated as follows:

\[ f_{cf} = \frac{pl(1000)}{B.D^2} \]

where:

- \( f_{cf} \) = Modulus of rupture, in mega Pascals.
- \( p \) = Maximum applied force indicated by the testing machine, in kilo newtons (kN).
- \( l \) = Span length, in millimetres.
- \( B \) = Average width of the specimen at the section of failure, in millimetres.
- \( D \) = Average depth of the specimen at the section of failure, in millimetres.

### 3.5.4 Measuring the structural damping ratio for a system containing 85-90% polymer concrete

This test does not identify the damping ratio of PC as a material property. The test is to identify the damping ratio of a structural system that consists of 85-90% PC. Furthermore, it reveals the damping ratio of PC that could affect the overall structural system-damping ratio. It also reveals the effect of the main source of damping, namely the resin, and how the resin volume fraction affects the overall structural damping ratio. A tap test was used to measure the damping ratio. In this test, a PC sample is set as a simple supported beam and tapped by hand. The frequency response is detected, and then the damping ratio is calculated using one of the methods available to calculate the damping ratio. Prior to describing the method in detail, the details of the samples and the mould will be described. The mould was designed using Pro/Engineer software. Figure 3.24 illustrates a detailed drawing of the mould assembly.
The following considerations were followed when designing the mould:

It must be thinner and longer than the flexural strength mould. It must be fully disassembled to consider the adhesion of the PC. In addition, ease of assembly and disassembly as well as safety must be carefully accommodated in the design. The dimensions of the samples produced by the mould were 500 mm × 50 mm × 25 mm.

The structural design of the sample is set up as a simply supported beam as it is quite similar to the structural design of the bases for precision tool machines. Figure 3.25 illustrates the PC sample and an accelerometer mounted to capture the frequency and the amplitude in Z direction. An accelerometer model 3192A, was connected to the amplifier model MODE4114B1. Both were made by Dytran Instruments, USA.
The amplifier was connected to the data acquisition system Model SCI-1000, made in Hungary by National Instruments, which fed the data to the computer to be analysed using data interface software (Lab view). Figure 3.26 shows the amplifier, data acquisition system and the computer. The measurement of the frequency and the amplitudes starts when the sample is tapped and the accelerometer captures the movements of the sample. The accelerometer converts the sample movements to a voltage signal that is amplified for transfer to the data acquisition system. It is then converted into a digital signal using a DAQ data card made by National Instruments, USA. The computer receives a digital signal to be analysed by software signal analysis, which presents the data in the time domain or frequency domain, as required.
The amplifier connected to both the accelerometer and data acquisition system to supply data to the computer.

There are different methods of estimating the damping ratio, using either time or frequency domain analysis. Logarithmic Decrement Analysis (LDA) can be used for the time domain analysis and Half Power Bandwidth (HPB) can be used for the frequency domain analysis. For this study, LDA was chosen to calculate the structural damping ratio. Figure 3.27 illustrates the LDA analysis. The decay in vibration amplitude, which is defined as the natural log of the ratio of the size of two peaks, m cycles apart, can be estimated using Equation 3.2.

\[
\delta = \frac{1}{m} \ln \left( \frac{y_n}{y_{n+m}} \right) \quad \text{(3.2)}
\]
where $y_n$ is the amplitude of the $n$th cycle and $y_{n+m}$ is the amplitude of the $n+m$th cycle. The damping ratio can then be found from Equation 3.3.

$$\zeta = \frac{\delta}{2\pi} \quad (3.3)$$

The time domain can be obtained with a tap test obtained using Excel, as shown in Figure 3.28. The structural damping ratio can be calculated using the LDA method.
3.5.5 Measuring coefficient of thermal expansion (CTE) for PC composite

The only difference in measuring CTE for PC as a composite material is the sample size. The samples used for flexural strength testing were identical to those used for the CTE test, with the same equipment and formulas. Figure 3.29 illustrates the custom-built device in a schematic diagram with the set-up for measuring the CTE of PC composite.
Figure 3.29 Schematic diagram of CTE custom-built device.
Chapter 4

Optimization of polymeric matrix

4.1 Introduction

This chapter describes the effect of resin’s chemical composition on the CTE, damping factor, flexural strength, tensile strength and hardness through procedures to determine the optimum resin for use as a resin binder in PC for the bases of precision tool machines. The nature of the application requires a PC with high damping, low CTE and high flexural strength. The main source of the properties required by the application is the resin. Resins of various ratios of styrene: ARAPOL and methyl methacrylate (MMA): ARAPOL (36% UPE and 33% styrene) were made and the curing kinetics were followed using viscosity measurements and exothermic reaction temperature profiles. The resins were studied using dynamic mechanical analysis and in-house thermal expansion measuring devices. In addition, resin kinetic analysis was considered in resin-aggregate mixing performance to achieve the lowest viscosity for the optimized resin. The exothermic reaction temperature profile was also considered, to
determine the lowest level to avoid thermal degradation and thermal stresses in order to eliminate a potential fatigue point. This ensured that the nominated resin was equipped with superior mechanical strength and the optimum capacity to damp the unwanted vibration generated during operation of the precision tool machine, and to have a low CTE.

4.2 Curing of unsaturated polyester resin

The curing of UPE resin is a radical polymerization process involving three steps: initiation, a propagation process, and a termination step. The initiator used was MEKP, which produces a radical species at room temperature. The unsaturated polyester used was ARAPOL. This is an industrial mixture of UP (67%) and styrene (33%). Another vinyl-based monomer (MMA) was added to this mixture to reduce the viscosity and improve the mixing and potential mechanical properties. Cobalt octoate was used as a promoter in the curing process. During resin curing, the material went through three phases: viscous liquid, gel and solid. Each phase was imprinted by incentive conversions in the thermo-mechanical properties of the resin (Ramana Reddy et al., 2002)
4.2.1 Initiation step:

The initiation step starts with the production of free radical species from the initiator, followed by the first monomer, which may be the unsaturated bonds in the UPE, styrene or MMA monomers, based on their reactivity ratio. Figure 4.1 shows the initiation step.

![Initiation step for polymerization](image)

4.2.2 Propagation step:

The propagation step proceeds when the radical species produced in the initiation step reacts with double bonds in the unsaturated segments (Sidney, 1986) of the UPE (UP) or, MMA or styrene, as shown in Figure 4.2.
The presence of multiple unsaturated bonds in the UPE causes the growth of the resin in a cross-linked network form during this step.

4.2.3 Termination step:

The termination step ends the growth of the living radical ends in the growing segments of the polymeric network. This can occur through the reaction of two radical ends or the free radical species with growing ends. It produces a saturated bond, as shown in Figure 4.3.
The UPE resin curing process is an exothermic reaction. Thus the rate of this process is essential to the dissipation of the produced heat, and the integrity and uniformity of the resin produced. Here MMA monomers was used to reduce the reaction rate based on MMA reactivity ratio (Gan et al., 1994).
4.3 Rheological analysis

The purpose of the rheological analysis was to nominate the resin composition according to the optimization criteria for the resin binder in the PC used in bases for precision machinery. Rheological analysis was conducted to examine the effect of the addition of different proportions of styrene and MMA on the viscosity growth and exothermic temperature of the resin binder. According to the optimization criteria, the nominated resin should have the lowest viscosity growth and exothermic temperature.

4.3.1 The effect of styrene/UPE ratio

The effect of the styrene/UPE ratio on the curing rate was investigated by increasing the initial 30:70 ratio in ARAPOL and adding more styrene to the mixture. The addition of excess styrene reduced the initial viscosity of the mixture and increased the gel time in the curing process. The ARAPOL/styrene ratio was varied from 68:32 (68% ARAPOL) to 25:75 (25% ARAPOL) causing the viscosity growth rate to increase, as shown in Figure 4.4. The gel time increased from 1 minute to 28 minutes, as illustrated in Figure 4.6 based on gel time measurement. The method is described in Section 3.4.2.3 and the viscosity measuring method is described in 3.4.2.1.
Figure 4.4 Viscosity versus time for all ARAPOL/styrene compositions

Figure 4.5 Gel time versus ARAPOL volume fraction for ARAPOL/MMA composition.
4.3.2 The effect of MMA/styrene/UPE ratio

MMA is a monomer with a lower reactivity coefficient compared to styrene. It was used to reduce the initial reaction mixture viscosity and to reduce the curing rate of the resin (Gan et al., 1994). Comparing the viscosity increase of the curing MMA/styrene/UPE with that of styrene/UPE shows a further decrease in viscosity values and viscosity increase rates for the MMA/styrene/UPE with similar monomer/UPE ratios, as illustrated in Figure 4.7. This enhances the mixing efficiency with the initiator and promoter, producing a more uniform solid resin. It also enhances the mixing of the aggregate with the liquid containing the initial resin components in the PC formulation, by giving more time when the polymerizing mixture is still a flowing liquid. Gel time increased from 6 minutes to 210 minutes as MMA increased, as shown in Figure 4.5, while the gel time increased from 1 minute to 28 minutes as styrene content increased, as shown in Figure 4.6. The resin gel time outcomes supported the viscosity outcomes. This
reduction in viscosity growth rate and increase in gel time in ARAPOL/MMA compositions qualified the ARAPOL/MMA compositions as being appropriate in terms of the potential mixing enhancement of the aggregate with the liquid resin in the PC formulation. It also allows more time when the polymerizing mixture is still a flowing liquid resin to guarantee the wetting of all aggregates particles and therefore enhances the PC composite’s mechanical properties.

Figure 4.7 Viscosity versus time for all ARAPOL/MMA compositions
4.3.3 Exothermic temperature ARAPOL/Styrene compositions

The temperature of resin for ARAPOL/Styrene compositions was measured according to the method described in Section 3.4.2.1. Figure 4.8 illustrates the exothermic temperature profile for ARAPOL/styrene compositions. The ARAPOL/styrene ratio was varied from 20:80 (20% ARAPOL) to 75:25 (75% ARAPOL), which caused the exothermic temperature to increase from 21.3 – 144.4 °C. In other words, an increase of styrene increases the exothermic temperature. It is not desirable to have an elevated exothermic temperature as high as 144.4 °C or 103.13 °C, because a substantial increase of exothermic temperature can cause thermal degradation of resins, the formation of residual stresses and excessive shrinkage leading to crack formation.
Figure 4.8 Exothermic temperature profile during the curing of ARAPOL/styrene compositions.

4.3.4 Exothermic temperature ARAPOL/MMA compositions

The exothermic temperature profile is relatively lower in ARAPOL/MMA compositions than in ARAPOL/styrene compositions. Figure 4.9 shows the exothermic temperature profile for ARAPOL/MMA compositions. Increasing the ARAPOL/MMA ratio from 25:75 (25% ARAPOL) to 75:25 (75% ARAPOL) elevates the temperature from 0.5 - 123 °C. The increase in UPE increases the exothermic temperature while, the increase of MMA decreases the exothermal temperature.
Figure 4.9 Exothermic temperature profile during the curing of ARAPOL/MMA compositions.

4.4 Mechanical properties

The mechanical properties were investigated according to the optimization criteria for PC used for the manufacture of bases of precision tool machinery. All of the resin compositions were tested, and the resin that complied most fully with the optimization criteria was deemed the most suitable for the polymeric matrix. Rheological analysis was required to verify the final determination of the optimum resin.
4.4.1 Damping factor for polymeric matrix

Damping is the energy dissipation properties of a material or system under cyclic stress. The damping factor is a dimensionless measure describing how oscillations in a system decay after a disturbance. Many systems exhibit oscillatory behaviour when they are disturbed from their position of static equilibrium. In DMA the damping factor is the ratio of the storage modules to the loss modules. A high damping factor is the primary reason that thermoset resin is used as a binder in the PC for manufacturing the bases of precision tool machinery. This property constructs the functionality of damping the unwanted vibration in the bases of precision tool machinery. The damping factor was measured for all compositions of ARAPOL/styrene and ARAPOL/MMA using dynamic mechanical analysis (DMA), except for the 25% ARAPOL/styrene resin composition, because the resin sample was unsuitable for performing the DMA analysis, as shown in Figure 4.10. The reason is that increasing the styrene ratio causes a high degree of shrinkage and fracture in the resin after curing due to internal stresses. This makes it impossible prepare a sample suitable for assessing the mechanical properties. An isothermal frequency sweep for a dual cantilever was conducted in the frequency range of 1-200Hz, as precision tool machine work is in the range of 60-6000 rpm (Gale, 2008). In addition, the base structural design is a simple supported beam similar to the DMA experimental set-up. Figure 4.11 illustrates the DMA analysis of the results for the damping factor versus frequency for all compositions. The composition with the highest damping factor (tan delta), which was almost constant is 40% ARAPOL/MMA which reached a damping factor of 0.0458.
Figure 4.10 25% ARAPOL/styrene sample.

Figure 4.11 Damping factors of all resin compositions versus frequency plotted using universal V4 software from TA instruments.

Figure 4.12 shows the value of tan (δ) for all resins versus ARAPOL volume fractions. ARAPOL/styrene composition does not show a trend. With ARAPOL/MMA, an increase of ARAPOL volume fraction decreased the damping factor after reaching the maximum at 40% ARAPOL/60%MMA composition. The
damping factor decreased rapidly after reaching the maximum, as shown in Figure 4.12. At higher ARAPOL ratios the weak damping properties are mainly due to the highly cross-linked UPE network. In the case of resins containing UPE, MMA and styrene two parameters can contribute to the damping properties of the cross-linked polymer; (1) the length of uncross-linked segments in the MMA containing resins, and (2) the degree of cross-linking in both these resins. Higher ratios of MMA increase the length of the uncross-linked segments in UPE, increasing the loss modulus in the cross-linked network by allowing for a fraction of the mechanical energy to be absorbed in the free chain segments while shearing during the applied strain. This may explain the high damping factor of the MMA/ARAPOL composition.

![Figure 4.12 Damping factor of all resins at frequency of 100HZ, ARAPOL/styrene and ARAPOL/MMA compositions.](image-url)
4.4.2 Flexural strength

Flexural strength is an essential property for both the resin and the PC composite system, due to the structural design of the base for a precision tool machine, which acts as a simply supported beam. The resin with the highest flexural strength would have a positive reflection on the overall composite material performance, since resin is the backbone of the PC composite system. The flexural strength varies according to the amount of ARAPOL in each composition. Figure 4.13 illustrates the effect of ARAPOL volume fraction on UPE resin containing styrene and MMA on maximum flexural strength. ARAPOL/MMA compositions seem to have a higher strength than the ARAPOL/styrene compositions. This can be explained by the increase in the phase separation level as the styrene in ARAPOL/styrene is increased (Sanchez et al., 2000). The addition of excess MMA increases the flexural strength of ARAPOL/MMA from 73.7 to 128 MPa when it reaches the maximum at 40% ARAPOL/MMA, then it decreases even more than the ARAPOL/styrene. The reactivity coefficient for MMA is lower compared to styrene which is used initially to reduce the initial reaction mixture viscosity and reduce the curing rate of the resin (Gan et al., 1994). This situation enhances mixing initiator and promoter with the composition, and may be the reason for the ARAPOL/MMA composition having good mechanical properties compared to the ARAPOL/styrene composition (Rodriguez, 1993).
4.4.3 Tensile strength

Tensile strength was tested for different resin compositions, and the method is described in Section 3.4.1.1. Tensile strength was higher for ARAPOL/MMA than the ARAPOL/styrene compositions at the maximum. The tensile strength of ARAPOL/MMA followed a similar behaviour to the flexural strength. The highest strength was reached at 40% ARAPOL/MMA 58.6 MPa, as shown in Figure 4.14(a). The strain was lower for ARAPOL/MMA compositions than for ARAPOL/styrene, as can be inferred from Figure 4.14(b). The maximum strain was reached at the same resin composition at which maximum strength was reached. As shown in Figure 4.14, the strain for the 40% ARAPOL/MMA was 10%, which was low when compared with the same composition of 40% ARAPOL/styrene, which was 11.5%.
The modulus of elasticity was calculated. ARAPOL/MMA compositions demonstrate a higher level in modulus of elasticity than the ARAPOL/styrene compositions. Increasing ARAPOL or decreasing MMA can increase the modulus of elasticity at different levels of ARAPOL/MMA composition. Increasing the ARAPOL can increase the modulus of elasticity of ARAPOL/styrene compositions, except for the last point in 75%ARAPOL/styrene composition, which reduced rapidly as it was the lowest, as is shown in Figure 4.15.

Figure 4.14 Effect of ARAPOL volume fraction on (a) tensile strength, (b) strain for compositions containing MMA and styrene individually.
4.4.4 Coefficient of thermal expansion (CTE) for polymeric matrix

The most sensitive thermal property for a resin binder in PC is the CTE, which has a direct effect on precision tool machine accuracy. CTE is the key to control the behaviour of the PC base deflections, under thermal conditions, in the operational environment of the bases for precision tool machinery. The first order approximation of CTE in PC, as a composite, can be obtained using the mixing rule (Wong and Bollampally, 1999). This relationship can describe the influence of CTE resin on over all PC CTE.

\[
\alpha_c = \alpha_a \phi + \alpha_m (1 - \phi)
\]  

(4.1)
where $\alpha_c$, $\alpha_m$, and $\alpha_a$ are the CTEs of the composite, matrix resin, filler aggregate, and $\phi$ is the volume fraction of the aggregate respectively. The CTE of the polymeric matrix is usually the highest compared to the CTE of aggregates. In PC, the CTE of the mortar resin is usually 7 to 10 times higher than the CTE of the aggregate. Lowering the resin CTE to closer to that of the aggregate and other components such as cast iron inserts in the PC bases of precision tool machines produces a more homogeneous composite with uniform thermal expansion and less thermal stress, since CTE follows the rules for a mixture of composite material (Bruck and Rabin, 1999). CTEs were measured for numerous resin compositions of ARAPOL/styrene and ARAPOL/MMA at various proportions. Figure 4.16 shows resin samples prepared for CTE testing.

![Figure 4.16 Resin samples with various proportions of MMA, ARAPOL and styrene prepared for measuring CTE.](image)

Figure 4.17 and Figure 4.18 show the different thermal expansion behaviours for all compositions with linear behaviour in various grades.
Figure 4.17 Thermal expansion behaviour of different resins with different proportions of ARAPOL/MMA.

Figure 4.18 Thermal expansion behaviour of different resins with different proportions of ARAPOL/styrene.
These figures (Figure 4.17 and Figure 4.18) were used to calculate the CTE according to the method described in Section 3.4.1.3, in order to produce a clearer image of the behaviour of all compositions in relation to CTE. The CTE of all the compositions increased as ARAPOL volume fraction increased, as illustrated in Figure 4.19. This is due to the high CTE of the UPE in ARAPOL (67%). ARAPOL/MMA compositions have lower thermal expansion than ARAPOL/styrene compositions. This is consistent with reports of low CTE for PC with polymethyl methacrylate as binding resin (Blaga and Beaudoin, 1985). The thermal expansion of styrene-rich resin is higher due to the higher molecular packing factor in these resins, leaving only a small space for molecular expansion at increasing temperatures. The inclusion of MMA in the resin composition increases the spatial disorganization and lowers the molecular packing factor, allowing for the polymer chain expansion to be accommodated in the free space existing in the cross-linked network of the resin.

![Figure 4.19 CTE for all resin composition versus ARAPOL volume fraction (%).]
4.4.5 Hardness

Hardness was measured for a variety of resin compositions, according to the method described in Section 3.3.2. Figure 4.20 illustrates the relationship between ARAPOL volume fraction and Shore D hardness. Generally, it is reasonable to say that an increase in the ARAPOL volume fraction can decrease the hardness in the ARAPOL/MMA composition.

![Figure 4.20 ARAPOL volume fractions versus hardness shore D in ARAPOL/MMA composition.](image)

An increase in the volume fraction of ARAPOL does not indicate a trend in hardness Shore D for ARAPOL/Styrene compositions. The fluctuation in the increase and decrease of hardness Shore D with an increase in the ARAPOL volume fraction is shown in Figure 4.21.
Figure 4.21 ARAPOL volume fractions versus hardness shore D in ARAPOL/Styrene composition.

4.5 Conclusions

The composition with the highest damping factor of all the resins had 40% ARAPOL/MMA, which has a damping factor of 4.56%. The highest flexural strength was reached with the 40% ARAPOL/MMA composition, with 128 MPa and a low strain of 10%, as compared with the 40% ARAPOL/styrene, which was 11.5%. The lowest CTE was achieved with 25% ARAPOL/MMA (6.93×10^{-5} °C^{-1}), followed by 40% ARAPOL/MMA (7.98×10^{-5} °C^{-1}). The module of elasticity of the 40% ARAPOL/MMA was 759 MPa. The highest Shore D hardness for 25% ARAPOL/MMA was 86.6 and 85.5 for 40% ARAPOL/MMA. The result of the mechanical properties shaped the focus for the rheological analysis of the ARAPOL/MMA compositions, although the ARAPOL/styrene compositions
were not ignored. The effects of the UPE/styrene ratio in the ARAPOL/styrene and the UPE/MMA/styrene ratios in the ARAPOL/MMA composition were studied. It was concluded that the ARAPOL/MMA compositions were more suitable for consideration, since the mixing efficiency with the initiator, and the promoter produced a more uniform resin. In addition, it may also enhance the mixing of the aggregate with the liquid resin by allowing more time when the polymerizing mixture is still a flowing liquid. The exothermic temperature profile was relatively lower in the ARAPOL/MMA compositions than the ARAPOL/styrene composition. The lowest composition in terms of exothermic temperature and viscosity was the 25% ARAPOL/MMA, followed by the 40%ARAPOL/MMA. The mechanical properties of 25% ARAPOL/MMA were very low compared to the 40%ARAPOL/MMA. This resulted in the nomination of the 40%ARAPOL/MMA as the optimum binder for the PC use in the manufacturing of bases for precision tool machinery. It meets most of the optimisation criteria at a good level, while other resins met fewer of the optimisation criteria and failed some. Table 4.1 shows a comparison of the optimized resin with the published data on epoxy and UPE with various monomeric combinations. The epoxy mechanical properties are better than those of the UPE, as stated in Chapters 1 and 2. The average viscosity is very low compared to published data for both epoxy and UPE, as shown in Table 4.1, which is an advantage that can be used to enhance the mixing process when the resin is mixed with aggregates to obtain an PC composite with good mechanical properties. The reason for this is that the low viscosity of MMA is lower than water viscosity. In addition, the CTE of epoxy is less than the CTE of the optimized resin.
Table 4.1 comparison of the published data for epoxy and UPE with the optimized resin

<table>
<thead>
<tr>
<th>Property</th>
<th>The optimized resin</th>
<th>Epoxy from published literature</th>
<th>References</th>
<th>UPE from published literature</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Damping ratio</td>
<td>0.045</td>
<td>0.134</td>
<td>(Wang et al., 2008)</td>
<td>0.053</td>
<td>(Ray, 2009)</td>
</tr>
<tr>
<td>Tensile strength MPa</td>
<td>58.6</td>
<td>40-90</td>
<td>(IDES, 2013)</td>
<td>4.1-90</td>
<td>(IDES, 2013)</td>
</tr>
<tr>
<td>Flexural strength MPa</td>
<td>128</td>
<td>90-145</td>
<td>(IDES, 2013)</td>
<td>60-160</td>
<td>(IDES, 2013)</td>
</tr>
<tr>
<td>Viscosity, poise</td>
<td>1.5 (average)</td>
<td>20</td>
<td>(Vipulanandan and Paul, 1990)</td>
<td>40</td>
<td>(Vipulanandan and Paul, 1990)</td>
</tr>
<tr>
<td>CTE, 1/°C</td>
<td>7.93×10^{-5}</td>
<td>12×10^{-6}</td>
<td>(McKeown and Morgan, 1979)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chapter 5
Optimization of the polymer concrete filler composition system

5.1 Introduction

In this chapter damping properties, flexural strength and the CTE of PC are investigated for various PC filler compositions. These properties are the main parameters that can affect the accuracy of precision tool machines and the strength of the PC base. Six fillers (basalt, spodumene, fly ash, river gravel, sand and chalk) have been studied. PC samples were prepared with different compositions of aggregates containing the same resin volume fraction (aggregate 83% and resin 17%). A four-point flexural test was used to measure the flexural strength of the PC samples. The CTE for PC was measured using an in house custom-built device. The preliminary optimum composition with the highest flexural strength and the lowest CTE, was found to be basalt, spodumene and fly ash. The basalt, sand and fly ash composition was the second best. This second composition was considered for further optimization in terms of the resin volume fraction because of its ability to adopt a smaller amount of resin. Different samples of PC were prepared with a variety of resin volume fractions: 17%, 15% and 13%. The resin volume fraction
was demonstrated to have a significant effect on the CTE and flexural strength of PC. The effect of the resin volume fraction on the PC damping ratio was identified. It was found that 40% of the reduction in the PC structural damping ratio was due to the PC resin volume reduction of 4% (17-13%). The final optimized composition was basalt, sand and fly ash (filler 87% and resin 13%). ANSYS 13.0 software was employed to visualize the influence of PC compositions on the thermal expansion of the base and to show how it affected the level of precision of the tool machine.

5.2 Particles properties of aggregates

The aggregates’ true density, \( \rho_{\text{True}} (\text{g/cm}^3) \) was measured using a pycnometer, and their bulk density \( \rho_{\text{bulk}} (\text{g/cm}^3) \) was measured using a measuring cylinder. All methods have been described in Sections 3.3.3 and 3.3.4, respectively. The packing factor, \( (VP) \), was calculated based on the ratio of the obtained true and bulk densities. The fine aggregate (chalk, fly ash) particle size distributions were obtained using a laser scattering method facilitated by a Mastersizer X (Malvern Instruments, USA). Middle and coarse aggregate size distributions were obtained using sieve analysis. These methods were described in Sections 3.3.1 and 3.3.2, respectively. Figure 5.1 shows the particle size distributions for all aggregates. The BET (Brunauer, Emmett and Teller, 1938) active specific surface area of the aggregates was determined by nitrogen gas adsorption/desorption. The nitrogen sorption measurements were performed using Micromeritics ASAP 2010 (USA). The adsorption and desorption isotherms were recorded using an 89-point pressure table with 15 second equilibration intervals. The method is described in detail in Section 3.3.5.
Table 5.1 summarizes the measured aggregate properties and referenced aggregate properties, such as CTE ($a_s \, ^\circ C^{-1}$), for each filler (Brandt, 1988, Hummel, 1950).
Table 5.1 Properties of all sizes of aggregates: coarse, middle and fine filler.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\rho_{bulk}$ (g/cm$^3$)</th>
<th>$\rho_{true}$ (g/cm$^3$)</th>
<th>$V_p$ (%)</th>
<th>CTE Aggregate (°C$^{-1}$)</th>
<th>BET (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravel</td>
<td>1.63</td>
<td>2.61</td>
<td>62</td>
<td>11.2×10$^{-6}$ (Brandt, 1988)</td>
<td>0.12</td>
</tr>
<tr>
<td>Basalt</td>
<td>1.6</td>
<td>2.77</td>
<td>58</td>
<td>5.5×10$^{-6}$ (Brandt, 1988)</td>
<td>0.22</td>
</tr>
<tr>
<td>Spodumene</td>
<td>1.56</td>
<td>2.879</td>
<td>54</td>
<td>2.5×10$^{-6}$ (Hummel, 1950)</td>
<td>0.10</td>
</tr>
<tr>
<td>Sand</td>
<td>1.71</td>
<td>2.63</td>
<td>64</td>
<td>11×10$^{-6}$ (Brandt, 1988)</td>
<td>0.29</td>
</tr>
<tr>
<td>Chalk</td>
<td>1.35</td>
<td>2.69</td>
<td>50</td>
<td>10×10$^{-6}$ (Brandt, 1988)</td>
<td>1.60</td>
</tr>
<tr>
<td>Fly ash</td>
<td>1.33</td>
<td>2.71</td>
<td>49</td>
<td>5.2×10$^{-6}$ (Brandt, 1988)</td>
<td>1.02</td>
</tr>
</tbody>
</table>

The composition aggregate proportions were calculated using the Furnas method (Furnas, 1931). According to this method, the aggregate number of generations for particles is obtained based upon the ratio (K) of the biggest particle diameter and smallest particle diameter. The diameter ratio was calculated using data from Figure 5.1 and the volume of voids, which is equal to 100 - $V_p$ (%). $V_p$ can be seen in Table 5.1. Table 5.2 shows the average diameters of the biggest and smallest particles for each aggregate.
Table 5.2 Aggregate average diameters and volume voids.

<table>
<thead>
<tr>
<th>Aggregates</th>
<th>Equivalent diameter, (μm)</th>
<th>Volume voids (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravel</td>
<td>6150</td>
<td>38</td>
</tr>
<tr>
<td>Basalt</td>
<td>6570</td>
<td>42</td>
</tr>
<tr>
<td>Sand</td>
<td>335</td>
<td>36</td>
</tr>
<tr>
<td>Spodumene</td>
<td>328</td>
<td>46</td>
</tr>
<tr>
<td>Chalk</td>
<td>18.5</td>
<td>50</td>
</tr>
<tr>
<td>Fly ash</td>
<td>31</td>
<td>51</td>
</tr>
</tbody>
</table>

The K ratio for each composite is shown in Table 5.3. The number of generations obtained was 2.5-2.7 by using Figure 5.2. The number of generations must be in an integral number format according to Furnase method. The closest integral number to the number of generation obtained is 3. Three generations were therefore used for each composition.
Table 5.3 Ratios (K) of average smallest diameters to largest diameters for potential compositions.

<table>
<thead>
<tr>
<th>Aggregates</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravel/ Fly ash</td>
<td>0.005</td>
</tr>
<tr>
<td>Basalt/ Chalk</td>
<td>0.0047</td>
</tr>
<tr>
<td>Gravel /Chalk</td>
<td>0.003</td>
</tr>
<tr>
<td>Basalt/ Fly ash</td>
<td>0.0028</td>
</tr>
</tbody>
</table>

In Furnas theory, the ideal particle shape is assumed to be spherical (Furnas, 1931). The void volume fraction for three generations of particles can be obtained by applying K (0.0028 - 0.005) and the number of generations using Figure 5.3.
The volume of voids was within the range of 16 - 17 % in PC composition. According to the Furnas method, the diameter of the intermediate generation, \(D_2\), can be calculated using the following expression:

\[
D_2 = \sqrt{D_1D_3}
\]  \hspace{1cm} (5.1)

where \(D_1\) and \(D_3\) are the biggest and the smallest diameter of particle generations. \(D_2\) is calculated for all compositions as shown in Table 5.4.
### Table 5.4 Intermediate generation for the compositions.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Intermediate generation $D_2$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravel/ Fly ash</td>
<td>451.3</td>
</tr>
<tr>
<td>Basalt/ Chalk</td>
<td>348.6</td>
</tr>
<tr>
<td>Gravel /Chalk</td>
<td>337.3</td>
</tr>
<tr>
<td>Basalt/ Fly ash</td>
<td>451.3</td>
</tr>
</tbody>
</table>

All the intermediate generations, $D_2$, is bigger than both of the sand and spodumene largest particle sizes. The largest particle sizes of sand and spodumene were (335, 400 μm), as shown in Figure 5.1. This indicates that both spodumene and sand are suitable for any composition. The total absolute volume of fillers $V_0$ can be calculated using the following formula:

$$ V_0 = \frac{1}{1+V_1} + \frac{V_1}{1+V_2} + \frac{V_2^2}{1+V_3} \text{................................. (5.2)} $$

Where $V_1$, $V_2$ and $V_3$ are volumes of voids for the largest, intermediate and the smallest generations respectively. The relative volume of voids can be calculated using $1-V_p$.  

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### Table 5.5 Total absolute volume of fillers for each composition.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Absolute volume of all fillers, $V_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basalt/spodumene/fly ash</td>
<td>1.132</td>
</tr>
<tr>
<td>Basalt/spodumene/chalk</td>
<td>1.133</td>
</tr>
<tr>
<td>Basalt/sand/fly ash</td>
<td>1.098</td>
</tr>
<tr>
<td>Basalt/san/chalk</td>
<td>1.1</td>
</tr>
<tr>
<td>Gravel/sand/fly ash</td>
<td>1.089</td>
</tr>
<tr>
<td>Gravel/sand/chalk</td>
<td>1.090</td>
</tr>
<tr>
<td>Gravel/spodumene/fly ash</td>
<td>1.125</td>
</tr>
<tr>
<td>Gravel/spodumene/chalk</td>
<td>1.126</td>
</tr>
</tbody>
</table>

The total volume fraction occupied by the solid particles $V_f$ can be calculated using the following formula:

$$V_f = V_0 (1 - V_1^2)$$ .................................(5.3)
Table 5.6 Theoretical total volume fraction of solid for each composition.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Total volume of solid fillers, $V_f$ (%)</th>
<th>Total volume of void $(1-V_f)$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basalt/spodumene/fly ash</td>
<td>93.2</td>
<td>6.8</td>
</tr>
<tr>
<td>Basalt/spodumene/chalk</td>
<td>93.3</td>
<td>6.7</td>
</tr>
<tr>
<td>Basalt/sand/fly ash</td>
<td>90.4</td>
<td>9.6</td>
</tr>
<tr>
<td>Basalt/sand/chalk</td>
<td>90.5</td>
<td>9.5</td>
</tr>
<tr>
<td>Gravel/sand/fly ash</td>
<td>93.1</td>
<td>6.9</td>
</tr>
<tr>
<td>Gravel/sand/chalk</td>
<td>93.3</td>
<td>6.7</td>
</tr>
<tr>
<td>Gravel/spodumene/fly ash</td>
<td>96.2</td>
<td>3.8</td>
</tr>
<tr>
<td>Gravel/spodumene/chalk</td>
<td>96.3</td>
<td>3.7</td>
</tr>
</tbody>
</table>

The volume fraction of each aggregate component $P_i$ can be calculated using the following formula:

$$P_i = \left( \frac{V_i}{V_o} \right)$$

Where $V_i$ is the packing fraction of individual aggregates that can be obtained from Table 5.1. $V_o$ is the absolute volume of each composition and can be obtained from Table 5.5.

Equation 5.4 can be rewritten as follow:
\[ \Pi_i = \left( \frac{V}{V_o} \right)^{\frac{5}{5}} \] (5.5)

**Table 5.7 Volume fraction for each aggregate within its composition for all compositions.**

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Volume fraction of each aggregate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basalt/spodumene/fly ash</td>
<td>51, 47, 2</td>
</tr>
<tr>
<td>Basalt/spodumene/chalk</td>
<td>51, 47, 2</td>
</tr>
<tr>
<td>Basalt/sand/fly ash</td>
<td>52, 38, 10</td>
</tr>
<tr>
<td>Basalt/sand/chalk</td>
<td>52, 38, 10</td>
</tr>
<tr>
<td>Gravel/sand/fly ash</td>
<td>53, 38, 10</td>
</tr>
<tr>
<td>Gravel/sand/chalk</td>
<td>53, 37, 10</td>
</tr>
<tr>
<td>Gravel/spodumene/fly ash</td>
<td>55, 35, 10</td>
</tr>
<tr>
<td>Gravel/spodumene/chalk</td>
<td>55, 35, 10</td>
</tr>
</tbody>
</table>

This approach takes into account the volume of voids and provides a good indication of possible filler compositions (Furnas, 1931). However, it does not take into account particle shape and is to be used mainly for spherical bodies. Another approach is based on the wetting of the particle surface (Michaylov, 1989). According to this approach, the volume of resin can be identified using the following expression:

\[ V_r = V_o (S_1 V_1 + S_2 V_2) \delta_r K \eta_{f}, \] \( (5.5) \)
where $S_i$ is the specific surface area of aggregates, $\delta_r$ is the thickness of resin (1.5 - 2 μm), $K$ is a constant = 1.05 and $\eta_r$ is the relative viscosity at the temperature of moulding with a reference temperature of 20°C. The smallest aggregates are not taken into account (Michaylov, 1989). The main problem with this approach is that it does not take into account voids between aggregates.

Theoretical calculations can provide valuable information about the composition of solid filler in terms of better packing. However, the volume fraction of the mortar can be identified only after a set of trial tests on the PC materials. The results obtained by using the Furnas method were implemented as a start in the trial procedure. Numerous trials were run to obtain the aggregate composition and the amount of resin that keep the resin surfaced for all the composition samples at the end of the moulding operation. It was found that the best aggregate proportions for the PC mixture were as follows:

Fine aggregate 8.3%, coarse aggregate 49.8%, middle size aggregate 24.9% (v/v) and 17% (v/v) resin. The preparation of the sample of PC was described in Section 3.5.1.

### 5.3 Thermal expansion of composite material

When heat is applied to a material, there is a change in temperature $T_1 \rightarrow T_2$ with a corresponding change in volume $V_1 \rightarrow V_2$. If the difference between temperatures is small, the change in volume is in direct proportion to the temperature change by a coefficient, $\beta$, which is called the coefficient of volumetric thermal expansion. The corresponding coefficient for the linear case is the
coefficient of the linear thermal expansion, $\alpha$. If the substance is isotropic, the relationship between linear and volumetric coefficients of thermal expansion is as follows: $\beta=3\alpha$ (Touloukian, 1977). Thermal expansion of any composite material in general, where filler is dispersed in a matrix, depends upon the following factors (Touloukian, 1977, Chawla, 1988):

- Thermal expansion of matrix, $\alpha_m$
- Thermal expansion of dispersed filler, $\alpha_f$
- Volume fraction of filler or matrix, $V_f, V_m$
- Isothermal bulk modulus of filler, $B_f$
- Isothermal bulk modulus of matrix, $B_m$
- Shear modulus of matrix $G_m$

The component is considered to be incompressible, when $B_f$ and $B_m$ values are infinite. The coefficient of thermal expansion for a composite material $\alpha_c$ may be determined using the rule of mixture (Chawla, 1988, Touloukian, 1977) according to the following expression:

$$\alpha_c = \alpha_f V_f + \alpha_m (1-V_f)$$

It seems that the reduction of CTE of the matrix and filler reduces the CTE $\alpha_c$ of the composite material. In addition, the volume fractions of resin and filler have an effect on $\alpha_c$. To reduce the CTE of PC, an experiment in each direction was
feasible. However, the one with the highest feasibility was the resin reduction, since the resin is the component that has the highest CTE (7.98 ×10^{-5}°C^{-1}).

5.4 Results and discussion

Aggregate surface morphology, particle size distribution, voids and resin volume fraction are synergic and fatalistic parameters in governing the thickness and shape of interfacial adhesion bonding (IAB) between PC particles. The main driver of the thermal and mechanical properties of PC such as CTE and flexural strength is the interfacial adhesion bonding between particles. The thermal properties of particles and aggregate proportions affect the overall CTE of PC (Xu et al., 1994). Figure 5.4 shows a PC sample demonstrating the failure mechanism that went through the interfacial adhesion bonding between filler particles, i.e. the polymeric matrix.

Figure 5.4 SEM of failed PC sample: the failure mechanism is going through the interfacial bonding between filler particles, in this case fly ash.
Eight compositions were investigated and compared in order to select the one with the highest flexural strength and the lowest CTE. Figure 5.5 shows PC samples for all compositions.

![Figure 5.5 Samples of polymer concrete of different compositions.](image)

The preliminary suggestion of optimum composition for a precision machine base application was basalt, spodumene, and fly ash, as shown in Table 5.8. The flexural strength was 22.85 MPa, due to the fact that crushed basalt increases the flexural strength of concrete (Kilic et al., 2008), basalt surface contains rough textures (rough surface) due to the crushing process. Fly ash also increases the flexural strength of polymer concrete (Rebeiz and Craft, 2002).
Table 5.8 Aggregate compositions used in the PC formulations in this study and their flexural strength and CTE.

<table>
<thead>
<tr>
<th>No.</th>
<th>Compositions</th>
<th>Flexural Strength (MPa)</th>
<th>Deflection (mm)</th>
<th>CTE (°C⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Basalt, spodumene, fly ash</td>
<td>22.85</td>
<td>1.458</td>
<td>10.0×10⁻⁶</td>
</tr>
<tr>
<td>2</td>
<td>Basalt, sand, fly ash</td>
<td>22.41</td>
<td>1.05</td>
<td>14.9×10⁻⁶</td>
</tr>
<tr>
<td>3</td>
<td>Basalt, spodumene, chalk</td>
<td>21.57</td>
<td>1.007</td>
<td>10.3×10⁻⁶</td>
</tr>
<tr>
<td>4</td>
<td>Basalt, sand, chalk</td>
<td>20.05</td>
<td>1.00</td>
<td>16.1×10⁻⁶</td>
</tr>
<tr>
<td>5</td>
<td>Gravel, sand, fly ash</td>
<td>18.92</td>
<td>0.94</td>
<td>14.6×10⁻⁶</td>
</tr>
<tr>
<td>6</td>
<td>Gravel, spodumene, chalk</td>
<td>18.22</td>
<td>0.90</td>
<td>12.6×10⁻⁶</td>
</tr>
<tr>
<td>7</td>
<td>Gravel, spodumene, fly ash</td>
<td>16.27</td>
<td>0.97</td>
<td>12.5×10⁻⁶</td>
</tr>
<tr>
<td>8</td>
<td>Gravel, sand, chalk</td>
<td>16.92</td>
<td>0.92</td>
<td>18.8×10⁻⁶</td>
</tr>
</tbody>
</table>

Spodumene, which comes from lithium mining, has textures attributable to the mining process. Figure 5.6(a) shows spodumene particles indicating that the microstructure of spodumene is in the form of crystallite layers (J.Graham, 1975). The layers may partially separate to some extent at the beginning and the end of the layer during mixing. This allows the mixture of fly ash-resin to flow between the spodumene layers, basalt textures and microspore cavities, since fly ash is the first filler mixed with the resin. Spodumene and basalt are then added to the PC mixture. This condition results in higher adhesion bonding between the polymeric matrix and the aggregates.
Figure 5.6 SEM images of (a) Spodumene: with hard and sharp textures containing layers, (b) Sand: round and smooth, (c) Fly sh: spherical shape and smooth surface, (d) Chalk: irregular shape with texture.

In addition, fly ash particles have a spherical shape, a smooth surface and a micro size, as shown in Figure 5.6(c). This leads to low viscosity at the time of mixing the fly ash with the resin, as compared to chalk, as illustrated in Figure 5.7. This indicates the high flow ability and filling capability of the fly ash-resin mixture. The basalt texture and the layers of spodumene facilitate the formulation of a highly adhesive interfacial bonding between the polymeric matrix and the aggregate. This is a possible explanation for the high flexural strength of the first composition.
The first composition scored the lowest of CTE, $10.0 \times 10^{-6} \, ^\circ\text{C}^{-1}$. All aggregates have a low CTE (Hummel, 1950, Brandt, 1988), and the lowest value is spodumene, as shown in Table 5.1. The flexural strength of the second composition (basalt, sand and fly ash) was 21.41 MPa. Sand has a higher BET active surface area than spodumene, as shown in Table 5.1, and less textural roughness on the surface, as shown in Figure 5.6(b). In addition, there are no layers in the microstructure of the sand particles to give extra grip, which may be the reason for the slightly reduced flexural strength. The second composite had a higher CTE, by approximately 50%, than the first. This is due to the sand CTE effect, which is almost three times more than the spodumene CTE and two times more than the fly ash CTE, as shown in Table 5.1. The main reason for the reduced flexural strength in the third composition (basalt, spodumene and chalk) is that the chalk particles have a more active surface area than fly ash, as shown in Table 5.1. This indicates that more resin is required for efficient wetting. Furthermore, the chalk resin mixture...
provides less flow ability and filling capability than the fly ash resin mixture, as shown in Figure 5.7. The reason for this is the irregular shape of the chalk particles and the number of sharp corners (rough surface), as shown in Figure 5.6(d). This results in higher viscosity during the mixing, which leads to the formation of a lower adhesive bonding mechanism on the surface of the aggregates compared to fly ash. This level of gripping adhesion leads to a reduction of the flexural strength. The CTE for the third composition is close to the first composition, due to the presence of spodumene, which has the lowest CTE, as shown in Table 5.8.

The fourth composition (basalt, sand and chalk) suffers because of the chalk and sand that both share responsibility for low flexural strength and high CTE, for the reasons explained previously. Replacing basalt with river gravel in the fifth composition results in a reduction in flexural strength. River gravel has a smaller BET surface area and a smoother surface than basalt, which may be the reason for less adhesion and a reduction in flexural strength. River gravel increases the CTE of the fifth composition, as shown in Table 5.8. It has a higher CTE than other aggregates, as shown in Table 5.1.

The presence of river gravel, chalk and sand in a PC composite system reduced the flexural strength and increased the CTE at various levels for different compositions. This condition was due to the CTE of the particles, as well as their morphology, and may have resulted in an interfacial bonding that had less adhesion between particles than basalt, spodumene and fly ash composition.
The second composition was nominated for further optimization in terms of resin volume fraction. This step was owing to its ability to accommodate a resin volume fraction of less than 17%. The reason is that sand has a high packing volume due to its rounded particle shape. In addition, the particle shape of fly ash is spherical and have high compaction. Figure 5.8 shows the effect of a reduction in the resin volume fraction on the CTE of PC.

![Figure 5.8 CTE of PC composite versus resin volume fraction.](image)

Decreasing the resin volume fraction results in a decrease in the CTE of PC, since the resin has the highest CTE \((7.98 \times 10^{-5} \, ^\circ\text{C}^{-1})\) in PC components. It was noticed that the layer thickness of segregated fine aggregate, which appears in the upper level of the sample during the PC sample vibration process, is affected by the resin volume fraction in PC. Figure 5.9 reveals that increasing the volume fraction of the
resin will increase the layer thickness of the segregated fine aggregate-resin mixture.

![Figure 5.9 Layer thickness of segregated fine aggregate for different resin volume fraction.](image)

**Figure 5.9 Layer thickness of segregated fine aggregate for different resin volume fraction.**

PC composite follows the rule of mixture regarding composite mechanical properties. Reducing the resin by 4% reduced the CTE of PC by approximately 31%. The other side effect of resin reduction is flexural strength. Figure 5.10 demonstrates that a reduction in the amount of resin by 4% reduces the flexural strength by approximately 36%. This is because the amount of resin that fulfils the interfacial adhesion bonding (IAB) between particles is reduced (Knab, 1972). The lowest flexural strength is 13 MPa for 13%, which is still acceptable for building a base. The base cross-section is sufficient to cope with the relatively low flexural stress, considering the small machine weight in comparison to the base size.
5.5 Effect of resin volume fraction on polymer concrete damping

To identify the effect of the resin volume fraction on the PC damping ratio, a structural damping test was conducted in order to provide an indication of the damping ratio of a structural system that contains a PC sample which occupies 80-90% of the experimental system. A tap test was conducted for PC samples composed of basalt, sand and fly ash containing 20, 17, 15 and 13% resin volume fractions. The method of testing was described in Section 3.6.4. A PC sample containing 20% resin volume fraction was added for the purpose of elucidating the effect of resin on the damping ratio of the PC. Figure 5.11 shows the time domains for different samples of PC with 17, 13, and 20% resin volume fractions.
The damping ratio was calculated for 12 PC samples according to logarithmic decrement analysis (LDA), as described in Section 3.6.4. Each set of four samples had a different amount of resin. Figure 5.12 shows the damping ratio for each set at the same time. The results indicate that the amount of resin is the main key control in relation to the damping ratio of PC.
The results indicate that approximately 40% of the reduction in the structural damping ratio is due to the PC resin volume reduction of 4% (17-13%). These results do not represent the material damping ratio of PC as a material property, but provide an indication of the effect of the amount of resin in a PC composite on the structural damping ratio of the experimental system. This result is consistent with other research that used epoxy as a resin binder in a composite material (Bai et al., 2009).

5.6 Results validation

To have a realistic understanding of the effects of filler compositions and resin volume fraction on the base, CAE software ANSYS 13 was adopted. The software was also used to reveal the effects of optimized properties on the functional performance of the PC base in relation to the precision tool machine accuracy level.
within the boundary of a thermal load obtained from an industrial environment. Figure 5.13 shows the CAD model of a CNC grinding tool machine. The CAD model was used including the frame, the main part of headstock and the main servomotor. The mass point feature in ANSYS 13.0 was utilized to avoid any complications that might arise during the analysis due to assembly complexity. It was also used to show the effect of all machine components on the base without considering assembly issues.

Figure 5.13 CAD model of a CNC grinding tool machine and the base, in transparent mode, demonstrating insert supports using yellow arrows.

The mass point feature allows the effect of heavy components on the precision tool machine base, without having a complex assembly in the CAD model during the simulation. Figure 5.14 shows centroid determinations for each assembly group individually.
Figure 5.14 Centroid determinations for each individual group of components (tagged by red).

A centroid of each sub-assembly, linked to the contact area of the base using the mass point feature at two mass points (A-600 kg and B-300 kg), is shown in Figure 5.15.

Figure 5.15 The main mass point to be included in the simulation.
Figure 5.16 shows the outlet coolant, inlet coolant and environment temperatures during the time of operation for the base of a CNC grinding tool machine. The method of measuring temperature was the same as that used in monitoring the temperature profile for the resin, which is described in Section 3.4.2.2. The framed area in Figure 5.16 was selected as the boundary condition at the peak point for the environmental temperature (24.8 °C) and outlet coolant temperature (22.3 °C), to be taken from the frame and applied as a boundary condition in the simulation.

![Figure 5.16 Outlet, inlet and environment temperatures versus time under operational conditions for a CNC grinder tool machine.](image)

The environmental temperature was 24.8 °C when applied to the outside of the base and the coolant outlet temperature was 21.5 °C and applied on the inside of the base where the water splashed on the base after cooling the tool in the grinding operational conditions. Figure 5.17 shows the temperatures and the areas that were applied.
Figure 5.17 Temperatures and the areas where they were applied on the base.

The temperature distribution on the base was obtained using steady-state thermal analysis in ANSYS 13.0 CAE software, as shown in Figure 5.18.

Figure 5.18 Temperature distribution on the base of the CNC grinder tool machine.
Constraints were applied to the stands where the machine was fixed to the ground. Material was assigned according to the material properties. Structural analyses under thermal conditions were run using ANSYS 13.0, and Figure 5.19(a) illustrates the directional structural deformation (Z-direction) of the base for the first composition (basalt, spodumene, fly ash). The thermal conductivity, which could not be measured, was obtained from the literature 2.8 (w/mk) (Demirboga and Gul, 2003). It was expected to be very close to the PC material. The modules of elasticity obtained from the compression test were 14.6 GPa, the compression test being in accord with AS12002.9-1986, as described in section 3.5.2. The most effective part of the base is the rails that hold the moving components and are an essential part of the guiding system of the CNC grinder tool machine in the operational environment. Maximum deformation was 25 μm on the wall base, concentrated on an ineffective component (in terms of precision performance), which is a small portion of the base located on the walls (approximately 2% of the base). The variation in deformation of the rails on one side was approximately 2 μm. The variation in deformation between the two sides of the rails was approximately 0.1 – 0.5 μm. The last composition in ranking: river gravel, sand and chalk, had almost double the thermal expansion compared to the first composition, as shown in Table 5.8. Figure 5.19(b) exhibits the directional deformation on the base containing the last composition. Maximum deformation is 45.5 μm and 75 % of the upper half of the base has been deformed nearest to the maximum. Variations in deformation on the rails are 3 – 5 μm. Variations in deformation between the two sides of the rails are approximately 1 – 3 μm.
Figure 5.19 Structural deformations under thermal conditions (a) first composition (basalt, spodumene, and fly ash), (b) last composition (gravel, sand, chalk).

Figure 5.20(a) shows that the directional structural deformation of the base for the second composition (basalt, sand, fly ash, resin volume fraction is 17%), and the maximum deformation in Z direction is 30.2 μm. Rail variations on one side are 1.5 – 2 μm. Variations in deformation between two sides of the rails are 0.2 – 0.34 μm.

Figure 5.20 Structural deformations under thermal condition (a) PC resin amount 17% (b) PC resin amount 13%. 
Figure 5.20(b) exhibits the directional structural deformation of the base for the composition (basalt, sand and fly ash) with a 4% reduction in resin volume fraction. The maximum deformation in Z direction for the base is 18 μm. Rail variations are 0.13 – 0.34 μm. Variations in deformation between the two sides of the rails are 0.011 – 0.06 μm. These variations are the smallest, and hence can be ignored, since they are less than 1 μm for both one side and two sides of rails variations in deformation. Table 5.9 illustrates all measurements in one domain for a clear comparison.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Resin volume fraction (%)</th>
<th>Maximum deflection (μm)</th>
<th>Variation in deformations on the rails in one side (μm)</th>
<th>Variation in deformations between two sides of rails (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basalt, spodumene, fly ash</td>
<td>17</td>
<td>25</td>
<td>2</td>
<td>0.1-0.5</td>
</tr>
<tr>
<td>Gravel, sand, chalk</td>
<td>17</td>
<td>45.5</td>
<td>3-5</td>
<td>1-3</td>
</tr>
<tr>
<td>Basalt, sand, fly ash</td>
<td>17</td>
<td>30.2</td>
<td>1.5-2</td>
<td>0.2-0.34</td>
</tr>
<tr>
<td>Basalt, sand, fly ash</td>
<td>13</td>
<td>14.6</td>
<td>0.31-0.13</td>
<td>0.11-0.06</td>
</tr>
</tbody>
</table>

5.7 Conclusions

The utilization of aggregate morphology, and the thermal and mechanical properties of particles, resulted in an optimum PC being obtained for the base of a precision machine. In conclusion:
- The optimum composition is basalt, sand and fly ash (87% filler and 13% resin), which has the lowest CTE and acceptable flexural strength.
- A reduction in resin diminishes the negative effect of sand in relation to the final CTE and the resulting flexural strength is acceptable for the application.
- A reduction in resin by 4% from 17% down to 13% reduces the damping ratio by a 40% reduction of the structural damping ratio of PC.
- When any aggregate of the optimum composition is replaced with another aggregate (gravel, sand and chalk), it results in the PC composition suffering a further reduction in flexural strength with an increase in CTE. The main reason for this was that the morphological and thermal properties of particles affect the interfacial adhesion bonding behaviour in the PC composite system.
- The optimum composition is extremely cost-effective compared to the first composition. Sand is 90% less expensive than spodumene and a 4% resin reduction reduces the cost of the composite by more than 4%. Resin is the most expensive component in a PC composite system.
- Based on simulation studies, the optimum composition reduce the variations in deformation of rail bases to a sufficiently low level for them to be ignored. This enhancement of the operational conditions for precision tool machinery improves the level of precision and achieves more precise products.

Comparing the damping ration of optimized PC with cast iron which is 0.418%(Orak, 2000) it was found that the optimized PC higher than cast iron by 6 times approximately.
Table 5.10 shows a comparison of the optimized PC with the published data of PC-epoxy based and PC-UPE. The properties of PC-epoxy are higher than the PC-UPE, but the PC-epoxy is quite expansive compared to PC-UPE. In addition, the property of optimized PC is better than PC-UPE published data.

<table>
<thead>
<tr>
<th>Property</th>
<th>The optimized PC</th>
<th>PC-Epoxy from published literature</th>
<th>References</th>
<th>PC-UPE from published literature</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Damping ratio,%</td>
<td>2.4</td>
<td>4.36–5.34</td>
<td>(Li et al., 1996)</td>
<td>2.21</td>
<td>(Cortés and Castillo, 2007)</td>
</tr>
<tr>
<td>Flexural strength, MPa</td>
<td>22.41</td>
<td>50</td>
<td>(Czarnecki, 1993)</td>
<td>15</td>
<td>(Czarnecki, 1993)</td>
</tr>
</tbody>
</table>
Chapter 6

Optimization of moulding technology

6.1 Introduction

Aspects of moulding technology have a great effect on the quality and productivity of the polymer concrete used to manufacture the base of precision tool machine. In this chapter, the results and the analysis are both presented of an experimental investigation on the effects of moulding technology on mechanical strength and maturity of polymer concrete. Those aspects are as follows:

- Effect of voids population on compressive strength of polymer concrete.
- Influence of DMA amount and moulding temperature on maturity, mixing process and the strength of matrix domain.
- Mixing technology and its influence on mechanical properties of PC.

Enhancing certain aspects of moulding technology could lead to an elevation of the mechanical strength of PC that may assist in producing PC with a high level of compliance with the optimisation criteria for PC used in manufacturing bases for precision tool machinery.

### 6.2 The effect of the number of voids on the compressive strength of polymer concrete

Voids can affect the mechanical properties of PC and a high number of them is not desirable. Reducing the voids population can enhance the mechanical properties of the concrete (Knab et al., 1983) as the microstructure and location of voids have a negative effect on mechanical strength. They can also influence the cracks that emanate and propagate, resulting in failure of the composite material (Zhu et al., 2011). In order to reduce the number of voids, a vibration table was used to induce a high level of compaction for PC. There is a range of frequencies available on a vibration table that used for achieving high level of aggregates compaction in PC. Each frequency induces a specific level of compaction on a PC sample which has a direct influence on mechanical properties. To find the optimum frequency, PC samples were prepared using various frequencies during the compaction stage and were tested for compressive strength. The PC sample with the highest compressive strength is the one with the lowest voids population and the optimum compaction.
Three accelerometers were mounted on the vibration table to capture the frequency and the amplitude in three directions of X, Y and Z. Frequency was measured in the same way as measuring the structural damping ratio described in section 3.6.4. The only difference is that the calculation of the damping ratio is not required. Frequency and amplitude are the main aims of this experiment. Figure 6.1 illustrates the experiment set up to measure frequency and amplitude of the vibration table.

Figure 6.1 Experimental setup for measuring the frequency and the amplitude of a vibrating table.
The frequency controller of a vibration table starts at 0 Hz and finishes with 50 Hz. The measuring of the frequency and amplitudes starts at 0 and goes up to 32 Hz. When 32 Hz is reached, the accelerometer magnetic attachment will not remain attached to the vibration table and falls down. Table 6.1 shows the result measurement of frequency and the amplitude of the vibrating table. The results of the measurements indicated that real frequencies are very close to the set values indicated by the vibrating table. The direction of oscillation does not seem to have an effect on the value of frequencies, as shown in Figure 6.2.

Table 6.1 The frequency and amplitude of the vibrating table.

<table>
<thead>
<tr>
<th>Vibrating table control reading</th>
<th>Frequency in X direction, Hz</th>
<th>Amplitude in X direction, mm</th>
<th>Frequency in Y direction, Hz</th>
<th>Amplitude in Y direction, mm</th>
<th>Frequency in Z direction, Hz</th>
<th>Amplitude in Z direction, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10</td>
<td>0.256</td>
<td>10</td>
<td>0.11</td>
<td>10</td>
<td>0.02</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>0.45</td>
<td>12</td>
<td>0.263</td>
<td>12</td>
<td>0.047</td>
</tr>
<tr>
<td>14</td>
<td>14</td>
<td>0.66</td>
<td>14</td>
<td>0.672</td>
<td>14</td>
<td>0.08</td>
</tr>
<tr>
<td>16</td>
<td>15.875</td>
<td>0.188</td>
<td>15.88</td>
<td>1.767</td>
<td>15.875</td>
<td>0.147</td>
</tr>
<tr>
<td>18</td>
<td>17.062</td>
<td>1.21</td>
<td>17.06</td>
<td>7.5</td>
<td>17.062</td>
<td>1.067</td>
</tr>
<tr>
<td>20</td>
<td>18.9375</td>
<td>2.7169</td>
<td>18.94</td>
<td>9.8</td>
<td>18.9375</td>
<td>2.162</td>
</tr>
<tr>
<td>24</td>
<td>23.5</td>
<td>2.24</td>
<td>23.5</td>
<td>8.9</td>
<td>23.5</td>
<td>2.814</td>
</tr>
<tr>
<td>26</td>
<td>25.56</td>
<td>1.66</td>
<td>25.56</td>
<td>8.5</td>
<td>25.56</td>
<td>3.66</td>
</tr>
<tr>
<td>28</td>
<td>27.5</td>
<td>2.7</td>
<td>27.5</td>
<td>8.71</td>
<td>27.5</td>
<td>5.4637</td>
</tr>
<tr>
<td>30</td>
<td>29.312</td>
<td>1.0189</td>
<td>29.31</td>
<td>8.06</td>
<td>29.312</td>
<td>5.8</td>
</tr>
<tr>
<td>32</td>
<td>30.375</td>
<td>0.766</td>
<td>30.38</td>
<td>7.499</td>
<td>30.375</td>
<td>13.853</td>
</tr>
</tbody>
</table>
As the frequency increases, the amplitude increases, particularly in Z direction for frequencies more than 30 Hz, as shown in Figure 6.2.

![Graph showing the relation between amplitude and set frequency for the vibration table.](image)

**Figure 6.2** Relation between the amplitude and set frequency for the vibration table.

Different frequencies were applied during the packing operation of the PC samples using the vibration table. The mould containing the PC sample was fixed on to the vibration table and vibration applied to the PC sample as shown in Figure 6.3. When the liquid resin reached the surface of the PC sample in the cylindrical mould and the bubbles stopped coming out of the surface resin, the vibration table was stopped.
The PC sample was then left for 28 days to cure at the ambient temperature. Upon completion of curing, the compressive strength was tested for each PC sample according to Australian standard AS 1002.9 – 1986 “Method of testing concrete: Part 9, Method for determination of the compressive strength of a concrete specimen”. The method of testing is described in 3.6.2. The optimum frequency for vibration and for producing a PC sample with the highest compressive strength was found to be 18.9375 Hz (20 Hz by the vibration table switch controller), which resulted in 109 MPa compressive strength for basalt, sand and chalk composition, as shown in Table 6.2.
Table 6.2 Vibrating time and compressive strength of PC samples

<table>
<thead>
<tr>
<th>Set frequencies on vibration table controller, Hz</th>
<th>Vibration time (min)</th>
<th>Frequency Measured, X direction (Hz)</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>10</td>
<td>15.875</td>
<td>98</td>
</tr>
<tr>
<td>18</td>
<td>12</td>
<td>17.062</td>
<td>93.5</td>
</tr>
<tr>
<td>20</td>
<td>16</td>
<td>18.9375</td>
<td>109</td>
</tr>
<tr>
<td>22</td>
<td>15</td>
<td>21.375</td>
<td>106</td>
</tr>
<tr>
<td>24</td>
<td>22</td>
<td>23.5</td>
<td>97</td>
</tr>
<tr>
<td>26</td>
<td>20</td>
<td>25.56</td>
<td>81</td>
</tr>
</tbody>
</table>

6.3 Identification of maximum moulding duration as a function of moulding temperature and DMA content in resin binder

Moulding time is the time required to mix PC with aggregates, then pour the PC mixture into the mould and vibrate the mould using a vibration table until the vibration process finished. The Dimethyl aniline DMA (promoter) amounts, MEKP initiator, monomer reactivity ratio and moulding temperature are the key controls of resin rheological behaviour from the commencement of mixing aggregates with the resin to the end of the final operation in vibrating the mould (Ganglani et al., 2002, Yang and Suspene, 1991). In addition the DMA (promoter) amount affects the mechanical and rheological properties of the resin (Ganglani et al., 2002, Yang and Suspene, 1991) and hence has an effect on the PC composite’s mechanical properties. During the moulding time the resin is required to be in a liquid state. This enhances the wetting of the aggregate particles, improves the mixing operation and increases particle settlement to achieve good mixing and compaction. As a result there is a reduction in the number of voids. The overall
result is the enhancement of the mechanical properties of PC. To achieve such a result, it is important to identify the DMA amount required correlate with the moulding temperature, and the moulding time. Extending the moulding time up to gel stage could cause some damage such as crack initiation during the compaction process, or result in a low level of mixing, both leading to reduced mechanical properties of PC.

6.3.1 Effect of DMA (promoter) contents on temperature rise during curing

The effect of the DMA content on temperature rise during curing was investigated. DMA content exerts an influence on the temperature of resins during their curing. Resins without DMA did not exhibit any recordable rise of temperature while resins with DMA had temperature increases up to 120 °C for 0.3% of accelerator. The increase of DMA content leads to an increase in the exothermic maximum resin temperature during the curing and shortens the time needed for a temperature rise, as shown in Table 6.4. The method of measuring temperature was described in Section 3.4.2.2.
6.3.2 Effect of DMA contents on viscosity growth during resin copolymerization

The effect of DMA on the curing rate was investigated by increasing the initial content of 0.001 in 40% ARAPOL/60% MMA resin composition and adding more DMA to the mixture. The addition of DMA increases the initial viscosity of the mixture in the curing process. The amount of DMA was varied from 0.001 to 0.003, causing an increase of the viscosity growth rate, as shown in Figure 6.5. The method used to measure viscosity was described in Section 3.4.2.3.
Figure 6.5 Viscosity of resins versus their curing time for a variety of DMA content.

Varying the DMA content is another measure that is used to demonstrate the effect of DMA content on the time required for the resin to reach the maximum viscosity as shown in Figure 6.5. An increase in the DMA content and the moulding temperature decrease the time required for the resin maximum viscosity to be reached, as shown in Figure 6.6.
Figure 6.6 Time to the maximum temperature of 40% ARAPOL/60% MMA resins with different contents of DMA for various moulding temperatures.

The time required for the resin to reach maximum viscosity is essential knowledge when manufacturing bases for precision tool machinery. The reason is both the PC mixing and the moulding tasks should be accomplished prior to maximum viscosity being reached by the resin binder (640 cP), which is on the verge of the gel point. A drastic increase in viscosity hinders mixing, resulting in PC material not to be mixed and moulded efficiently. The effect of both temperature and DMA amount will be combined in a convergence on the PC base’s mechanical properties and curing behaviour. The relation between time of viscosity build-up $t$ (min), temperature $T$ ($^\circ$C) and DMA content $C$ (%) can be described in the following empirical equation:
\[ lnt = 6.42 - 5.1C - 0.069T \] ..............................(6.1)

Using the above equation, the DMA amount was calculated which is compatible with the known moulding temperature, as illustrated in Table 6.3.

Table 6.3 Recommended DMA content for different moulding temperatures.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMA (%)</td>
<td>0.3</td>
<td>0.29</td>
<td>0.27</td>
<td>0.26</td>
<td>0.25</td>
<td>0.23</td>
<td>0.22</td>
<td>0.21</td>
<td>0.19</td>
<td>0.18</td>
<td>0.17</td>
</tr>
<tr>
<td>T(°C)</td>
<td>20</td>
<td>21</td>
<td>22</td>
<td>23</td>
<td>24</td>
<td>25</td>
<td>26</td>
<td>27</td>
<td>28</td>
<td>29</td>
<td>30</td>
</tr>
<tr>
<td>DMA (%)</td>
<td>0.14</td>
<td>0.13</td>
<td>0.11</td>
<td>0.10</td>
<td>0.09</td>
<td>0.07</td>
<td>0.06</td>
<td>0.04</td>
<td>0.03</td>
<td>0.02</td>
<td>0.0</td>
</tr>
</tbody>
</table>

By using Figure 6.6, the recommended DMA content for the various moulding temperatures in Table 3.3 can be validated. For example, the recommended DMA for 10 °C moulding temperature is 0.27 %. In Figure 6.6 the time required to reach the maximum measurable viscosity (640 cP) is 73 minutes at 10 °C and 0.3 % DMA. When DMA is reduced, the time for reaching the maximum viscosity increases at a particular temperature. This indicates that the time for reaching the maximum viscosity is greater than 73 minutes when the DMA amount is less than 0.3% at 10°C, the time considered when the DAM amount calculated for Table 6.3 is 75 minutes approximately. The required time for moulding is 40-50 minutes, depending on the size of the PC base and the complexity of the design. The recommended DAM correlated with temperature in Table 6.3 provides 15-35% extra time to the required time as an extra precaution to guarantee that the moulding operation takes place when the resin is at the low viscosity level. This is to avoid reaching the verge of gel time, especially during compaction stage that
may initiate undesirable micro-cracks in the polymeric matrix that can propagate
during the solidification of the base, since UPE resin has high shrinkage compared
to epoxy.

6.3.3 Effect of DMA content on curing behaviour of resin binder

The effect of DMA on curing behaviour was investigated using Differential
Scanning Calorimetry (DSC) and the Borchardt and Daniels equation (Borchardt
and Daniels, 1957). Their kinetic approach facilitates the evaluation of activation
energy ($E_a$), the pre-exponential factor ($Z$), heat reaction ($\Delta H$), reaction order ($n$)
and rate constant ($K$) from a single scanning. The results of the DSC tests
demonstrate the difference between samples with and without DMA, as shown in
Figure 6.7. Thus, the presence of DMA could shift the peak of the DSC curves to
higher temperatures resulting in a stronger exothermal reaction, as the area under
the DSC curve is bigger in the case of the sample with 0.3% DMA. The presence of
DMA, as expected, changes the parameters of the Borchardt and Daniels model.
However, the variation is not too high as can be seen in Table 6.6. The method of
conducting the DSC analysis was described in section 3.4.2.4.
Table 6.4 Parameters of Borchardt and Daniels model for 40%ARAPOL /60%MMA resins with different contents of DMA.

<table>
<thead>
<tr>
<th>DMA content, %</th>
<th>Reaction order, n</th>
<th>Activation energy, kJ/mol</th>
<th>Log Z, log(1/min)</th>
<th>Heat of Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.95</td>
<td>204</td>
<td>30.4</td>
<td>84</td>
</tr>
<tr>
<td>0.1</td>
<td>2.84</td>
<td>203</td>
<td>30.1</td>
<td>98</td>
</tr>
<tr>
<td>0.2</td>
<td>2.74</td>
<td>193</td>
<td>28.9</td>
<td>100</td>
</tr>
<tr>
<td>0.3</td>
<td>2.65</td>
<td>195</td>
<td>29.5</td>
<td>101</td>
</tr>
</tbody>
</table>

Figure 6.7 DSC curves of 40%. ARAPOL/60%MMA resins without DMA (solid curve) and with 0.3% of DMA (broken curve).

The heat of reaction is increased as DMA (promoter) amount is increased as shown in Table 6.4. This result supported the outcome of the exothermal
temperature profile as shown in Figure 6.4, the peak exothermic temperature increase as DMA amount is increased.

6.3.4 Effect of DMA contents on resin binder mechanical properties

The effect of DMA on the resin’s mechanical properties was investigated using flexural strength, tensile strength and elongation. The method of measuring flexural strength and tensile strength testing was described in Sections 3.4.1 and 3.4.1.2. Tensile strength, flexural strength and elongation all decreased with an increase in DMA content, as illustrated in Table 6.5. Thus the strength of resins with 0.3% DMA is 25% lower than resins without DMA. Elongation is also reduced by 18% and these results are in partial agreement with those of Ganglani et al. (Ganglani et al., 2002). This is attributed to the formation of micro-cracks, possibly caused by the excessive exothermal reaction in the presence of the accelerator as the exothermic reaction peak temperature increased as DMA amounts increase as shown in Figure 6.4. This caused non-uniform temperature distribution across the resin sample and initiated non-uniform shrinkage when the resin solidified. It should be noted that this effect may be much greater with larger volumes of resin, because of the scale factor. Taking into account the very low fraction of resin (the micro-layer thickness between aggregates) in PC composite material and the substantial heat exchange between the matrix and the fillers, the detrimental effect of DMA on mechanical properties ought to be much lower.
### Table 6.5 Mechanical properties of resins with different volume fractions of DMA.

<table>
<thead>
<tr>
<th>DMA content, %</th>
<th>0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus of elasticity (MPa)</td>
<td>705</td>
<td>759</td>
<td>798</td>
<td>675</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>60.2</td>
<td>58.6</td>
<td>51.9</td>
<td>43.6</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>10.1</td>
<td>9.3</td>
<td>8.1</td>
<td>8.3</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>130</td>
<td>128.2</td>
<td>119.3</td>
<td>109.5</td>
</tr>
</tbody>
</table>

#### 6.4 Optimization of mixing technology of PC

The main purpose of concrete mixing is to achieve a uniform mixing of all materials (ACI, 1972). Mixing technology is an important parameter for a PC with low binder content. Poorly mixed PC not only fails to meet the requirements for workability but also affects the PC’s mechanical properties. Three mixing technologies were investigated for a specific aggregate composition (basalt, sand, flay ash).

The first mixing technology (MT1) started by mixing the fine aggregate with 75% of the resin, followed by the medium-sized aggregate and then, finally, the coarse aggregate was added to the main mixture with the rest of the resin. The second mixing technology (MT2) began by mixing 20% of the resin with coarse aggregate. The micro-filler was separately mixed with 30% of resin and then added to the coarse aggregate resin mixture. The rest of the resin was separately mixed with the medium-sized aggregate and then mixed with the main mixture. In the third mixing technology (MT3), all aggregates were premixed and then mixed with the
A traditional concrete mixer was used to mix the PC for all the mixing technologies. A time of 15 minutes was used for all three mixing technologies. Samples to measure flexural strength were prepared for each mixing technology. A four-point flexural strength test was conducted according to the Australian standard AS 1012.11-2000 method of testing concrete. The method used to test flexural strength was described in Section 3.6.3. Table 6.6 shows the flexural strength for all mixing methods. MT1 proved to be the most effective for basalt, sand and fly ash, and flexural strength reached the maximum of 22.6 MPa.

<table>
<thead>
<tr>
<th>Mixing technology</th>
<th>Composition</th>
<th>Flexural Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT1</td>
<td>Basalt, sand, fly ash</td>
<td>22.53</td>
</tr>
<tr>
<td>MT2</td>
<td>Basalt, sand, fly ash</td>
<td>19.23</td>
</tr>
<tr>
<td>MT3</td>
<td>Basalt, sand, fly ash</td>
<td>20.32</td>
</tr>
</tbody>
</table>
6.5 Conclusions

This chapter has examined aspects of moulding technology. Each has a different effect and influences the mechanical properties and curing behaviour of PC by various means. The optimum frequency when operating the vibration table to prepare a PC sample is identified as 18.9375 Hz. With this frequency, the PC samples produced the highest compressive strength. An empirical relationship connecting the moulding temperature and the DMA content was obtained using rheological analysis of the resin with various amount of DMA. A table showing moulding temperatures in the range of 8-30°C with DMA amounts in the range of 0-0.3% was constructed. It was found that increasing the DMA fraction in the resin binder has a slightly negative impact on the mechanical properties and increases the curing rate as well as the exothermic temperature profile. Various mixing technologies were investigated in order to obtain one that produces the PC with the highest flexural strength. It was found that MT1 produces a PC sample with 22.53 MPa, which is the maximum flexural strength.
Chapter 7

Influence of moisture on the thermal and mechanical properties and curing behaviour of a polymeric matrix and PC composite system

7.1 Introduction

Moisture is mainly free water found in voids and capillary pores in the filler aggregate (Lamond and Pielert, 2006). Water also can be found as ingress moisture in the carbon fibres used in PCs containing fibre-reinforced polymer (Tuakta and Buyukozturk, 2011). All forms of moisture are dependent on the humidity level of the local conditions and the micro-climate of the material. This subject is covered in the research literature with the primary focus on (i) the moisture sorption of the resin binder after the curing is completed and the PC composite is implemented in a specific application, for example in underwater constructions (Y. Ohama, 1997) and (ii) the pre-existing water in aggregates, where 3% of pre-existing water in aggregates has been found to reduce the compressive strength of PC by a half (Fontana and Reams, 1985). It was also reported that PC consisting of unsaturated polyester, styrene and acid monomers, such as maleic anhydride, are successfully
polymerized in the presence of 5% water with improved mechanical properties compared to the same PC without maleic anhydride containing the same level of moisture (Ignacio et al., 2008).

Ignacio et al. (2008) state that water molecules trapped inside ionic cages interfere less with the overall curing process for UPR (Ignacio et al., 2008). The remainder of other effects of pre-existing water in aggregates on PC’s mechanical and thermal properties and curing behaviour for both PC and resin binder that have not received adequate attention to date. In this chapter the influence of moisture on the thermal and mechanical properties, and the curing behaviour of a polymeric matrix and PC composite system are investigated.

7.2 Sample preparation

Sample preparation for the resin domain and the PC composite is reported in the following sections.

7.2.1 Resin domain

The resin investigated was made from commercial general purpose, unsaturated polyester (AROPOL) (67% unsaturated polyester dissolved in 33% styrene) and obtained from Huntsman Chemical Company (Australia). Methyl methacrylate (MMA) was obtained from Degussa (Australia), cobalt octoate and dimethyl aniline (DMA) from Alfa Aesar (USA), and methyl ethyl kenton peroxide (MEKP), commercially known as NR20, from Nuplex Industries (Australia). A resin sample was produced by mixing 3:2 (v/v) UPE/MMA. 0.8% cobalt octoate (promoter), 0.2% DMA (accelerator) and 2% (v/v) MEKP (initiator) were then added to this
mixture, in this sequence by hand for 1-2 minutes. 1% - 5% (v/v) of water was then added to the mixture to investigate the effect of the moisture content on the curing process and the final polymeric matrix properties.

7.2.2 Polymer concrete composite

The basalt and sand used as filler aggregates were from Roca, and the fly ash was supplied by Cement Independent Australia. The PC mixture contained fine aggregate 8.3%, coarse aggregate 49.8% and medium-sized aggregate 24.9% (v/v). Aggregates were heated using a vacuum chamber to produce zero moisture aggregates. When the zero moisture aggregates were produced, a moisture check was conducted using moisture analyzer MD 150 from Starous, Germany, thus ensuring that the level of moisture was zero. 1% - 5% (v/v) of water was then sprayed on to each aggregate individually. Each aggregate was left for 30 minutes with the mixer on to evenly distribute the water. Samples of aggregates were checked for moisture levels using the same moisture analyzer. When the mixing of water and aggregates was accomplished, 17% (v/v) of resin was mixed with the aggregates. The mixing was continued for 20 minutes to ensure the best mixing of all particles with the resin, and in order to maximize the resin interface with the pebbles. The mixture of resin-aggregate was poured into a rectangular mould assembly (100 × 100 × 300 mm), which had been coated with a release agent consisting of a gel coat and PVA to prevent adhesion to the steel mould. The PC sample was cured for 28 days at ambient temperature. The flexural strength of the PC samples was measured using a Snitech 60/D universal testing machine according to Australian standard AS 1012.1, and the testing method is described in Section 3.6.3. A German ALPHA 3, with two columns, was used to measure the compression strength of the PC according to Australian standard AS1012.19.2.2000, and the method of testing is described in Section 3.6.2. The PC
samples for compression were prepared following the same procedure as was used for the flexural strength test. The mould used for the compression strength PC sample was cylindrical, 100 mm in diameter and 300 mm in length. A sample with the same measurements as those used for flexural strength testing was used for measuring the CTE of the PC composite system, using the method described in Section 3.6.5.

7.3 Results and discussion

A series of experiments was conducted to investigate the water–resin interaction in the polymeric matrix domain and in a PC composite system. The thermal and mechanical properties and the curing behaviour of UPE were computed and analysed. The thermal and mechanical properties of the PC composite systems were measured and explained. The moisture of the aggregates used for PC was measured and then the solubility of the water in the components of the resins studied was examined. MMA water solubility was 1.2%, as shown in Table 7.1. If more than 1.2% water was added and mixed with MMA, the water appeared to be undissolved in the MMA. When mixing stopped, the water droplets stayed at the bottom of the beaker. ARAPOL (UPE dissolved with 33% styrene) was immiscible, as water was emulsified when it was added and mixed with the resin. This indicates that up to 60% of added water (1.2% MMA water solubility) will be dissolved in the MMA when the percentage of water is 1%. The rest of the water will mainly evaporate during the copolymerization process due to the heat generated by the exothermic reaction. When 1% of water was added to the resin composition, the share of MMA (1.2 ×60%) is 0.72 and the share of Dimethyl aniline (DMA)(0.2%×80%) is 0.03. According to Table 7.1, those components are the only soluble ones. The total ratio of soluble water is 0.75% in the resin. In
another words, the resin will reach saturation when the water added is 0.75% of the resin volume.

### Table 7.1 Water solubility for polymeric matrix contents.

<table>
<thead>
<tr>
<th>Component</th>
<th>Volume fraction in polymeric matrix</th>
<th>Water Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arapol UPE (dissolved in 33% styrene)</td>
<td>40%</td>
<td>Immiscible</td>
</tr>
<tr>
<td>Styrene</td>
<td></td>
<td>Immiscible</td>
</tr>
<tr>
<td>Methyl methacrylate (MMA)</td>
<td>60%</td>
<td>1.2%</td>
</tr>
<tr>
<td>Dimethyl aniline (DMA)</td>
<td>0.2%</td>
<td>(80%) Highly soluble</td>
</tr>
<tr>
<td>Cobalt octoate</td>
<td>0.8%</td>
<td>Immiscible</td>
</tr>
<tr>
<td>Methyl ethel kenton (MEKP)</td>
<td>2%</td>
<td>1%</td>
</tr>
</tbody>
</table>

7.3.1 **Measuring the level of moisture in aggregate**

The moisture test for the aggregate mixture, using a moisture analyser MD 150, indicated that there was a variation in the level of moisture, depending on the climate, and specifically on the local humidity. Figure 7.1 shows the level of moisture in the aggregate during the days of the week.
Figure 7.1 Moisture during the days of the week in aggregate used in polymer concrete.

7.3.2 Curing behaviour of the polymeric matrix

The effect of water on the resin curing process is assessed by DSC measurements. The Borchardt and Daniels model was used to analyse the results and calculate the reaction activation energy \( (E_a) \), pre-exponential or Arrhenius frequency factor \( (Z) \), heat reaction \( (\Delta H) \), reaction order \( (n) \) and rate constant \( (K) \) from a single scanning for the various water contents (Borchardt and Daniels, 1957). Their approach states that the curing reaction follows \( nth \) order kinetics and obeys the following equation:
\[ \frac{da}{dt} = K(T)[1 - a]^n \] .................................(7.1)

where \( \frac{da}{dt} \) is the reaction rate, \( a \) is the fractional (reaction progress %), \( K(T) \) is the specific rate constant at temperature and \( n \) is the reaction order. Borchardt and Daniels assume Arrhenius behaviour:

\[ K(T) = Z e^{-E_a/RT} \] .................................(7.2)

where \( Z \) is the Arrhenius frequency factor (1/sec), \( E_a \) is the activation energy (J/mol) and \( R \) is the gas constant 8.314 (J/mol °K). The DSC was conducted to examine the effect of moisture on the polymeric matrix. The method is described in Section 3.4.6. Utilizing a software feature supplied by TA Instruments (TA Speciality Library), resulted in the parameters of the Borchardt and Daniels model in Equations 7.1 and 7.2 being obtained, as shown in Figure 7.2.
Figure 7.2 DSC data processing using the TA Specialty library: inset time of 70% conversion at 60 °C versus water content.

The time of 70% conversion at 60 °C was estimated for various moisture contents, and Figure 7.3 show that an increase in water content generates an elevation in conversion time (time of reaction). An increase in water content leads to elevated activation energy and a reduction in the heat of the reaction as the moisture content rises. This illustrates the retardation effect of moisture during the curing, as shown in Table 7.2.
When water is added, a small portion of the water dissolves in the monomer (MMA), producing a mixture that is more stable and needs higher activation energy to initiate the chemical reaction. As a result, the heat of the reaction is reduced (see Table 7.2).
Table 7.2 Parameters of Borchardt and Daniels model for different resin moisture contents.

<table>
<thead>
<tr>
<th>Moisture content %</th>
<th>Reaction order, n</th>
<th>Activation energy [kJ/mol]</th>
<th>Log Z, log(1/min)</th>
<th>Heat of Reaction, [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.59</td>
<td>204</td>
<td>30.4</td>
<td>88.4</td>
</tr>
<tr>
<td>1</td>
<td>3.11</td>
<td>210</td>
<td>31.1</td>
<td>84.0</td>
</tr>
<tr>
<td>3</td>
<td>3.20</td>
<td>245</td>
<td>36.0</td>
<td>78.8</td>
</tr>
<tr>
<td>5</td>
<td>3.70</td>
<td>287</td>
<td>42.9</td>
<td>64.1</td>
</tr>
</tbody>
</table>

An increase in viscosity in the course of curing as the amount of moisture increased was supported by the DSC outcomes. Figure 7.4 shows that an increase in water content delays the increase in viscosity and increases the gel time. An increase in moisture content slows down the cross-linking process (copolymerization). Figure 7.4 inset shows that a greater time is needed to reach the gel stage as the moisture increase. A possible explanation for this outcome is that the energy generated by the exothermal reaction during the curing is consumed by the evaporation of water droplets, leaving less energy for the process of copolymerization. As a result, a lower curing rate is observed as the moisture content increases. The method of measuring viscosity was described in Section 3.4.2.1 and the method of measuring gel time was described in Section 3.4.2.3.
Figure 7.4 Viscosity increase for UPE containing various amounts of water: inset gel time versus water percentage in UPE.

7.3.3 Interaction of polymeric matrix with water

FTIR spectroscopy demonstrated the interaction between water and UPE functional groups. Figure 7.5(A) illustrates a peak between 3240 – 3270 cm\(^{-1}\). The C=O stretching is observed as a peak at 1717 cm\(^{-1}\) in unsaturated polyester resin (UPE) prepared with no initial water. The peak develops a shoulder at 1736 cm\(^{-1}\) with increasing water content. This is due to the formation of a different C=O bond strength between the water and carbonyl group in UPE, as illustrated in Figure 7.5(B). Hydrogen bonding can form between water and the oxygen in C-O in both ether and ester functional groups. This increases the peak width and intensity at 1142 and 1460 cm\(^{-1}\), as shown in Figure 7.5(C). This chemical interaction of water and UPE may be another factor in the weakening of the mechanical properties. The method of conducting FTIR spectroscopy was described in Section 3.4.2.7.
Figure 7.5 FTIR spectra of polymeric matrix prepared with 0, 1, 2, 4 and 5%v initial water, (A) O-H and C-H stretching peaks, (B) C=O stretching peak and (C) the range including C-O and C-H bending.

### 7.3.4 Thermal Gravimetric Analysis (TGA)

TGA analysis of the polymeric matrixes containing various amounts of water was conducted, using the method of testing described in Section 3.4.2.6. Figure 7.6 shows a peak below 250°C, a peak around 385 °C and two shoulders around 410 and 450°C. The initial weight loss can be assigned to the residual bound water from the resin. This process shows a peak in the derivative of weight loss (dw/dT) form of the data as shown in Figure 7.6. This peak shows a shift from 226 °C for the sample containing 1% initial moisture to 203, 181 and 168 °C for the 2, 3 and 5% initial moisture levels (Figure 7.6 inset). This shift may be due to two reasons: (i) the rate of weight loss depends on the mass transfer during the heating process, and this mass transfer depends on the water molecule diffusion through the pores in the resin. Higher initial moisture leaves a higher pore volume ratio and therefore causes the shift of the weight loss peak of the bound water to lower
temperatures. (ii) When a higher initial moisture level exists in the resin mixture, the water molecules have higher probability to participate in the curing process which is evidenced in the overlap of peaks at 385 and 450 °C in the resin decomposition region. Water may hydrolyse ester groups in UPE, especially at the high temperatures of the curing process, or terminate an active radical causing a less cross-linked network. The temperature of bound water evaporation exhibits the strength of interaction between water molecules and functional groups in the polymer network. Most water at lower ratio is completely soluble in the starting composition mixture, causing the imprinting of water molecules in the network.

Figure 7.6 TGA of polymeric matrix containing various amounts of water. The inset show an expended region of water evaporation weight loss (the graphs are scaled up by 1% for clarity).
Table 7.3 Peak temperatures for resins containing various amounts of water

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Moisture</th>
</tr>
</thead>
<tbody>
<tr>
<td>226°C</td>
<td>1%</td>
</tr>
<tr>
<td>203°C</td>
<td>2%</td>
</tr>
<tr>
<td>181°C</td>
<td>3%</td>
</tr>
<tr>
<td>168°C</td>
<td>5%</td>
</tr>
</tbody>
</table>

7.3.5 Resin domain mechanical properties

The effect of water content on the mechanical properties of the UPE resin was also examined. All methods used for the mechanical testing of the polymeric matrix were described in Section 3.4.1. The modulus of elasticity, Shore D hardness, flexural strength and tensile strength all deteriorate as water content increase, as illustrated in Figure 7.7.
This may be due to the pores left by water droplets or water vapour bubbles generated during the exothermic curing process, as seen in the SEM images in Figure 7.9, where pores act as stress concentration weak points in the resin structure and result in resin failure during loading tests. This is consistent with the work of Athijayamai et al (Athijayamani et al., 2009).
In the early stages of the reaction, water is distributed in droplet shapes because it is mixed with the resin domain. These water droplets prevent the active ends of the macromolecules forming a cross-linked network and, to some extent, prevent further copolymerization. The temperature builds up in the resin binder due to the exothermal reaction of UPE resin. The generated energy during the exothermic reaction is the main source of the chemical energy used to drive the polymerization process only when the moisture is 0%. A portion of the main chemical energy is taken to be used in evaporate the water in the course of curing. This leads to the formation of pores (voids) that affect the mechanical properties of the resins and delay curing. The evaporation of the water droplets creates voids with a spherical shape. Scanning electron microscopy was utilized to examine the microstructure of the fractured surface of the resins. Figure 7.10 exhibits a flexural test fracture surface, showing the hemispherical voids contain an active cross-linked network, ending at the edge of the half sphere. This interface forms a phase separation with a rough surface on the internal surface of the sphere.
Figure 7.10 Half sphere void exhibiting the nature of a void inner surface for polymeric matrix fracture (scale bar is 1 µm).

Figure 7.11 shows the voids formation during the early stages of curing the resin binder in liquid state.

Figure 7.11 Voids forming due to water existence at the early stage of curing resin containing 5% moisture.
The ratio of void volume to sample volume in resin (abbreviated as VV/SV) was calculated for each sample, using image-processing technology facilitated by Image J 1.42q software, and assuming that the polymeric matrix was uniform and that all voids were cylindrical. The cylindrical geometry goes along the material volume to accommodate all voids that exist in the material volume. The VV/SV was approximately three times greater than the actual moisture content in each sample. This is an indication of the effect of water droplet evaporation when the resin is at the gel stage. The vapour pressure was sufficient to significantly expand the volume of voids to double that prior to solidification. This phenomenal inflation has a deleterious impact on the mechanical strength of the resin domain, and explains why the mechanical strength drops so dramatically.

7.3.6 Dynamic Mechanical Analyses (DMA)

Measurement of the dynamic properties of the resin domain is essential when considering its usage as a binder in applications such as in PC in the production of a base for precision tool machine. Due to its damping properties, DMA testing was conducted to measure the damping factor (tan δ) and storage modulus. The method was described in Section 3.4.1.4. Figure 7.12(A) shows that the storage modulus declined for the resin as the water content increases. This behaviour can be explained by a dramatic change in morphology and by an increase in micro-cracks and voids as the water content increases. Figure 7.12(B) shows that the damping factor (tan δ) increases as the water content increases. The increase in micro-cracks and voids as the moisture content increases may also explain the increase in the tan δ (Panteliou and Dimarogonas, 2000). Micro-cracks and porosity are good dampers due to the inner friction inside a crack, which increases the damping properties.
7.3.7 Coefficient of thermal expansion (CTE) of polymeric matrix

The other important factor in applying UPE resin as a binder in PC for bases of high precision machines is its CTE. The CTE was measured for various resins containing different amounts of water. The method was described in Section 3.4.2.3. Figure 7.13 show that the increase in moisture content caused an increase in the CTE of the polymeric matrix. An increase in the number of voids results in a decrease in the resin density and modulus of elasticity as well as other mechanical properties, as demonstrated earlier. This leads to a reduction in the resistance of the material to the thermal expansion. Another parameter, the thermal conductivity of the polymeric matrix, also decreases as a result of the increase in the number of voids, which are full of air and reduce the heat dissipation inside the polymeric matrix. All of these occurrences converge to increase the CTE of the polymeric matrix as the water content increases.
7.4 Mechanical properties of polymer concrete composite material

Mechanical properties were measured for the PC, including flexure strength and compressive strength. The flexural strength test was conducted according to the AS 1012.11-2000 method of testing concrete described in Section 3.6.3. The flexural strength decreases catastrophically, with a loss of 99% of its initial value as the water content reaches 5%, as shown in Figure 7.14.
Figure 7.14 Flexural strength of polymer concrete composite system versus the percentage of moisture contents.

The BET surface area analysis was conducted for all aggregates using the method described in Section 3.3.5. Table 7.4 shows that the BET analysis indicates that extremely low microspores were detected for the aggregate in this study. Thus the added water to these aggregates is mainly present on the highly hydrophilic surface of these filler particles, affecting the strength of the bond with the resin.
A rather large proportion of the moisture in coarse aggregates is located at the surface of the aggregate. The thin micro-layer of the moisture affects the interfacial adhesion bonding between the aggregate and the polymeric matrix, as shown in Figure 7.15. An increase in the moisture content in the polymer concrete composite system increases the debonding of aggregates with the polymeric matrix and decreases the polymeric matrix strength when the moisture droplets are suspended in the middle of the interfacial bonding, as shown in Figure 7.15 those droplets become voids and delay the curing process of PC. This is the cause of the reduction in flexural strength, with an increase in the moisture content in the PC composite system. Figure 7.16 shows a PC sample containing 5% moisture, and there appear to be many debonding points between aggregate and resin.
Figure 7.15 Water distributions on a polymeric matrix and the interfacial bonding of matrix – aggregates in a polymer concrete composite system.

Figure 7.16 PC sample containing 5% moisture.
Compressive strength was measured according to the AS 1002.9 1986 method described in Section 3.6.2. The compressive strength decreases as the moisture increases, as shown in Figure 7.17 as the water percentage reaches 5%, the compressive strength diminishes by 55% of the initial value when the water percentage was zero.

![Graph showing compressive strength versus water percentage](image)

**Figure 7.17** Compressive strength of polymer concrete composite system versus the percentage of water content.

Based on Figure 7.18 and Figure 7.14, at the point when the moisture is 0.002% there is a very small decrease in compressive and flexure strength but this is negligible. It is, therefore, reasonable to suggest that when the moisture content is 0.002% or below, the overall aggregate composition is acceptable.

### 7.4.1 Coefficient of thermal expansion (CTE) of PC composite system

The CTE was measured in different samples of PC containing a variety of moisture contents using the method described in Section 3.6.5. The main
parameters influencing the CTE of the composite material are the volume fraction of both the fillers and the matrix. The CTE values for fillers and matrix, as well as the strength of the interfacial adhesion between the polymeric matrix and filler aggregate all affect the CTE of PC composite. The moisture can be located on the surface of the aggregates or emulsified in the polymeric matrix as a result of the mixing process, as shown in Figure 7.15. During the curing of a PC composite, the matrix is surrounded by aggregates that have low thermal conductivity (Demirboga and Gul, 2003), which results in intensifying most of the heat generated by the resin exothermic reaction contained within the resin domain itself. This results in the formation of more voids than when the resin domain interacts with moisture without aggregates. The strength of the PC composite system decreased due to the presence of the moisture. Decreasing the strength of a polymer concrete composite system will reduce the material resistance for thermal expansion caused by the temperature increase. This may explain why the CTE of the PC composite system increases as the water content increases, as illustrated in Figure 7.19. Based on Figure 7.1, at the point when the moisture is 0.002% there is a very small increase in CTE that can be ignored. When the moisture is 0.002% or below in the overall aggregate composition, since the change in CTE is very low. It is, therefore, reasonable to say that this is acceptable.
7.5 Conclusions

The curing behaviour of a polymeric matrix is substantially affected by moisture. Increasing the moisture causes an increase in the curing time and hence reduces the curing rate. Evaporation of the moisture also consumes the energy intake generated by the exothermic reaction originally required to cure the polymeric matrix. This results in a serious delay in the curing of the polymeric matrix. The thermal and mechanical properties are affected substantially by moisture in both the polymeric matrix and the PC composite system. The effect of moisture on the mechanical properties of the resin domain (flexural strength, tensile strength, modulus of elasticity and hardness) is large, and appears in flying colours in as shown in Figure 7.8. An increase in moisture decreases the mechanical strength of the resin domain due to the morphology change caused by the rapid increase in the void population and micro-cracks. The chemical energy generated by the
exothermic reaction and the moisture causes the inflation of voids at the gelation stage during the curing of the resin domain. This results in a doubling between the aggregates and the matrix of and an increase in the volume of voids to twice. The DMA results emphasize the increase in the damping factor with an increase in the water content of the resin domain. Increasing the damping factor is desirable for a specific application, such as PC for a precision machine. However, in view of the other unfavourable effects caused by water on the resin domain and the PC composite system, the elevated damping factor was ignored. The CTE of the polymeric matrix increases as the water content increases. The influence of moisture on the main mechanical properties of the PC composite system reveals that an increase in moisture would lead to a decrease in both the flexural and compressive strength at different rates. The flexural strength of the PC composite system loses 99% of its initial strength when the moisture content is 5%. The compressive strength loses 65% of its initial strength when the moisture content is 5%. The CTE of the PC composite strength decrease up to 50% as moisture content reaches 5%. FTIR spectroscopy scans show an interaction between water and the functional groups of the resins. TGA analysis enables the classification of water in resin binder based on the strength of the interaction between water molecules and functional groups in the polymer network. Increasing the water content increases the level of non-interactive water (bulk water) since the resin reaches saturation when the water content is 0.716 approximately. The existence of water in the particulate fillers can have a negative effect on both the productivity of a PC structure and the end-use mechanical properties. Drying of aggregate fillers affected by moisture should be an essential procedure in raw material preparation for PC. The allowable moisture must be as close to zero as possible. 0.002% may be an acceptable level of moisture in the aggregates used in manufacturing PC composite material.
Chapter 8

Maturity studies of polymer concrete

8.1 Introduction

The maturity method is a technique that accounts for the combined effects of time and temperature on the strength development of concrete (Carino and Lew, 2001). The concept of the maturity method is often used for cement concrete strength prediction. Both cement concrete and PC are composite materials, their main difference being the chemical nature of their mortar. PC mortar is a thermosetting binder, whereas the mortar of ordinary concrete is a cement paster. By definition, the maturity aspect for PC is therefore similar to ordinary concrete in some respects. Two common parameters, temperature and time, have the same effects on both PC and ordinary concrete in different forms and levels. The parameters driving the maturity operations of PC are directly connected to the curing of the thermosetting binder resin, which depends on the initiator, accelerator (Yang and Suspene, 1991), temperature of curing (Zheng et al., 1988) and monomeric reactivity ratio (Sanchez et al., 2000, Rodriguez, 1993). The curing of cement concrete depends on the temperature and chemical content of the cement paster (Carino and Lew, 2001). In addition, while watering enhances the strength development of cement concrete (Powers, 1948), the existence of water in the
aggregates in PC reduces the mechanical strength rapidly (Fontana and Reams, 1985). The common parameters for deriving the maturity of both PC and cement concrete are the maturing temperature and time. These parameters were used as the main drivers for the nominated maturity method. The maturing of the PC base takes a month or sometimes more when matured under the ambient temperature. This time is considered a long lead-time, and requires considerable storage space for thee tons of bases. Increasing the productivity and decreasing the lead-time would have a major impact on the cost of the PC base, and enhancing the maturity would have a positive effect on both productivity and the quality of PC base. In this chapter, the maturity method is identified. PC samples were heated for various periods of time at different temperatures, according to the maturity method. PC samples with different maturity conditions were tested for flexural strength. The datum temperature was calculated and a mathematical expression was obtained to predict the correlation of the relative flexural strength with maturity temperature.

8.2 Maturity method

The demand for a procedure accounting for the combined effects of time and temperature on strength development for different elevated temperatures grew as concrete material evolved. It had been proposed that the product of time and temperature could be used for this purpose for ordinary concrete (McIntosh, 1949, Nurse, 1949, Saul, 1951). These approaches led to the construction of a relationship, known as the Nurse-Saul maturity function:

\[
M(t, H(T)) = \int_{0}^{t} K(T(\tau)) d\tau \]

(8.1)
Where $M(t, H(T))$ is the maturity at age $t$ after temperature history $H(T)$, $\tau$ is the age of maturing, varying from 0 to actual age $t$, and $K(T)$ is the rate function which depends on the temperature $T$ of the concrete.

The equivalent age concept will be introduced later. For a concrete having a given maturity after a given temperature history, it is defined as the time during which the concrete should be placed at a reference constant temperature (usually average ambient temperature) to reach the same level of maturity. Mathematically, one can have:

$$M(t, H(T)) = M(t_e, T_r)$$

where $M(t_e, T_r)$ is the maturity at age $t_e$ at constant reference temperature $T_r$. $t_e$ is the equivalent age. By substituting Equation (8.1) in Equation (8.2) to obtain Equation (8.3):

$$M(t_e, T_r) = \int_0^{t_e} K(T_r) d\tau$$

From Equations (8.2), (8.3) and (8.4):
\[ t_e = \int_0^t \frac{K(T(\tau))}{K(T_e)} d\tau \] .................................................................(8.5)

The Arrhenius law can be used to determine equivalent age:

\[ K(T) = A \exp\left(\frac{-E_a}{R T}\right) \] .......................................................(8.6)

where \( E_a \) is the apparent activation energy of the process (in J/mol), \( T \) is the absolute temperature (in K), \( R \) is the universal gas constant (8.314 J/mol K) and \( A \) is the constant of the function. The associated equivalent age function can be obtained by substituting Equation 8.6 in Equation 8.5:

\[ t_e = \int_0^t A \exp\left[\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T(\tau)}\right)\right] d\tau \] .................................................................(8.7)

From this equation, there is a synergic effect of activation energy and temperature combined with time on the equivalent age of polymer concrete. Those mathematical indications can be validated by experimental results.
8.3 Datum temperature

Datum temperature can be defined as the temperature below which strength development ceases. A low datum temperature is an indication of low activation energy \((E_a)\). The catalyst amount may help in lowering the activation energy of PC resin binder (Lee et al., 1997). An increase in catalyst concentration will accelerate the reaction through the reduction of activation energy and lower the datum temperature.

8.4 Estimation of datum temperature

Maturity for ordinary cement concrete is defined as an integral of the curing period and temperature of cement concrete above a datum temperature, and is expressed by the following equations (Saul, 1951):

The rate constant

\[
K(T(\tau)) = T(\tau) - T_o
\]

where \(T_o\) is the datum temperature. When the maturing process is isothermal

\[
T(\tau) = T
\]

The maturity \(M_c\) according to the definition will be as follows:

\[
M_c = \int_0^t (T - T_o)d\tau
\]
\[ M_c = \sum (T - T_o) \Delta \tau \] (8.10)

where \( M_c \) = Maturity \((\circ C \cdot h)\) or \((\circ C \cdot d)\) of cement concrete at a curing period or age, \( t \) or \( \Delta \tau \) (hours or days), \( T \) = temperature \((\circ C)\) of maturing ordinary concrete, and \( T_o \) = datum temperature \((\circ C)\) below which there is no strength gain in the cement concrete, regardless of the curing period. Lee et al. considered \( \sqrt{\Delta \tau} \) as a replacement of \( \Delta \tau \) in Equation 8.10 because of more rapid progress of the setting or hardening process of rein binder in PC than the cement mortar in ordinary concrete (Lee et al., 1997). This modification in maturity equation is required due to the fact that greater strength development can be obtained in hardening process of PC than cement concrete. Therefore, maturity for PC \( (M_{pc}) \) can be expressed as follows:

\[ M_{pc} = \sum (T - T_o) \sqrt{\Delta \tau} \] (8.11)

For isothermal reaction \((T=\text{Constant})\)

### 8.5 Experimental studies of polymer concrete maturity

The reason for nominating flexural strength rather compressive strength was that a PC base acts as a simply supported beam and the main effective strength is therefore flexural strength. Compressive strength cannot be an efficient measurement, as the compressive load is very small compared to the flexural load. PC samples were prepared according to the method described in Section 3.6.1. To study flexural strength under various temperatures and times, samples were
matured using a Thermoline dehydrator oven TD-150, made in Australia. The samples were matured using the dehydrator oven at 35 and 50 °C. Small temperatures, such as 5°C, were achieved by using a 400L Samsung refrigerator. Ambient maturing took place at room temperature which was an average of 23.1°C. Various times of maturing were applied for each sample, starting with a minimum of six hours, to a maximum of two weeks. Once the maturing process was accomplished for a PC sample, a four-point flexural test was performed according to the Australian standard AS 1012.11-2000 to determine the flexural strength of the PC sample for a specific time and temperature. The test method was described in Section 3.6.3. All tests were run at ambient temperature half an hour after removing the samples from the oven or the fridge. A temperature check was performed on the PC sample prior to the flexural strength test. This procedure was to ensure that the PC sample had reached the thermal equilibrium with ambient temperature at the time of testing. Figure 8.1 shows the development of flexural strength for various maturing temperatures. Increasing the temperature increases the level of flexural strength development, which reduces the time for maturing.
Figure 8.1 Flexural strength of the PC as a function of maturing time at various maturing temperatures: ambient, 5 °C, 35 °C and 50°C.

The maximum flexural strength developed was 17.12 MPa, requiring 720 hours when the maturing temperature was 5 °C, as shown in Figure 8.1. The minimum strength measured at 50°C was 22.49 MPa, developed over 6 hours, as shown in Figure 8.1. Assuming that the rate of strength development for the first six hours is constant when the maturing temperature is 50 °C. Hence, the time required to develop 17.12 MPa at 50 °C is 4 hours and 34 minutes. By comparing this time with the time required for strength development at 5 °C, the following can be seen: by increasing the temperature from 5 °C to 50 °C, the time of the curing has decreased 157.65 times.
8.6 Relative flexural strength

The PC relative flexural strength in maturity operation can be defined as the ratio of the strength of a PC sample, matured at a particular temperature, and the maximum strength achieved by an identical PC sample for the same maturing temperature. The flexural strength was obtained for each temperature and time. The relative strength was calculated according to the definition. Figure 8.2 displays the relation between relative flexural strength and maturing time for 50°C. The experimental results indicated the elevated temperature effect on the rate of PC maturing.

![Figure 8.2 Relative strength of PC as a function of maturing time at 50 °C.](image)

The overall relation between maturing time \( t' \) (days) and relative strength \( \sigma_{rel} \) can be described empirically utilizing the following expression:
where \( \tanh \) is the hyperbolic tangent ( \( \tanh x = \frac{e^x - e^{-x}}{e^x + e^{-x}} \)), and \( k \) is the coefficient that can be calculated for a particular relative strength and time. Plotting the \( k \) coefficient per day for each temperature, as shown in Figure 8.3, revealed a relationship connecting \( k \) with the temperature.

Figure 8.3 revealed a relationship connecting \( k \) with the temperature.

The empirical relationship that governs the relative flexural strength with the maturing temperature and maturing time can be represented as following:

\[
\sigma_{rel} = \tanh(\sqrt{kt})
\]

where \( \sigma_{rel} \) is the relative flexural strength, and \( t \) is the maturing time. Using the data from Figure 8.3, we can express the relationship as:

\[
\sigma_{rel} = \tanh(\sqrt{(0.035T + 0.57)t})
\]
Figure 8.4 displays the experimental results of relative strength for each time and maturing temperature and the predicted results using the above formula for relative strength as a function of maturing time. All figures predicted and the experimental values are reasonably close.

Figure 8.4 Relative strength versus maturing time for 5°C maturing temperature (◊) experimental data and red curve predicted by the empirical formula.
Figure 8.5 Relative strength versus maturing time for 35°C maturing temperature (◊) experimental data and red curve predicted by the empirical formula.

Figure 8.6 Relative strength versus maturing time for 50°C maturing temperature (◊) experimental data and red curve predicted by the empirical formula.
The datum temperature can be estimated by utilizing the definition of datum temperature, and applying the boundary condition to Equation (8.13). The datum temperature is the temperature where the developed strength is zero, in other words, the relative strength is zero. This leads to K coefficient being equal to zero. To satisfy this condition:

\[ 0.035 T_o + 0.57 = 0 \] .................................(8.14)

\[ T_o = -(\frac{0.57}{0.035}) \] .................................(8.15)

\[ T_o = -16.3^\circ C \] .................................(8.16)

The ordinary concrete datum temperature is -10 °C (Bergstorm, 1953). Polymer concrete has a lower datum temperature than ordinary concrete, which also validates the Equation (8.13). The empirical Equation (8.13) allows obtaining the maturing time for a particular curing temperature at a certain known level of relative strength.

8.7 Moisture effect on the resin mechanical properties during maturing

The effect of moisture was investigated thoroughly and described in chapter seven, but the effect of maturity was not described there. The resin binder is the backbone of the composite material and seems to be the most effected by moisture during maturing, as shown in Figure 8.7. This effect is reflected on in the overall mechanical properties of a polymer concrete composite material. Samples of resins
was prepared in the same way that used in preparing resin sample for moisture study, the level of moisture was 1%. Resin sample were placed in oven for a day for various temperatures. It was observed that increasing the maturing temperature in presence of a low level of moisture resulted in an increased number of cracks and voids, as displayed in Figure 8.7.

During the curing of UPE resin there was a temperature build-up due to the exothermal reaction. The generated energy during the exothermic reaction was the fundamental source of chemical energy used in evaporating water that included in the resin in the course of curing. This resulted in the formation of pores (voids) that affected the mechanical properties of the resins. Evaporation of water droplets created voids with a spherical shape, as shown previously. This situation occurred

Figure 8.7 Moisture 1%, increase the maturing temperature increased the cracks and voids in UPE resin binder.
when the only energy available during the reaction was the exothermal energy. When the reaction energy combined with an external source of energy (maturing temperature) in the presence of moisture, the effect could be doubled or tripled, depending on power level of the combined energy source. The water droplets evaporated quicker and earlier during the curing of the resin with a higher pressure, causing more voids with a bigger volume and higher numbers of cracks as the temperature increased. Increasing the level of moisture brought an increase in the level of voids and cracks populations as shown in Figure 8.8. The main reason of using maturing process for polymer concrete is to enhance the mechanical properties and reduce the lead time for maturing. The presence of moisture induces a catastrophic result in terms of mechanical properties and undoubtedly increased the lead-time (maturing time).

![Image of UPE resin binder with different maturing temperatures](image)

**Figure 8.8** Moisture 2% shows a higher level of cracks and void populations in UPE resin binder.
8.8 Conclusions

The following conclusions were drawn from the results:

- An empirical mathematical expression was developed to predict the correlation of the relative flexural strength with temperature, as well as the time of curing.

- Datum temperature can be calculated using an empirical mathematical model.

- Increasing the temperature from 5 °C to 50 °C decreased the time of the curing by 157.65 times. Adapting the curing process in the production of a base could reduce the lead-time and enhance the quality.

- Existence of water diminishes the resin and PC mechanical properties two or three times as the maturing temperature increases.
Chapter 9

Conclusions

9.1 Introduction

The principal objective of this research was to optimize the PC composite materials to be used in manufacturing bases of precision tool machinery. Using composite materials for such an application in an optimized form can produce numerous enhancements to elevate the precision level of the machinery and increase the productivity of the PC base. The research work involved in the PC optimization was designed according to specific optimization criteria that were carefully identified according to application requirements. The main focus of this research was the optimization of the thermal and mechanical properties of PC bases, and the process of production of a PC for use in the manufacture of PC bases. For the optimization of the final properties, several critical performance parameters are nominated. The main parameters include the CTE, the damping ratio, and the flexural strength of the PC and resin binder. For optimization the process of the resin binder, the critical performance parameters are viscosity and temperature. Optimized PC offers improved mechanical, thermal and rheological properties. It can deliver desirable properties and produce further enhancement in the accuracy of precision tool machinery. The validation of the optimized PC base
using simulation demonstrates the potential to enable precision tool machines to produce enhanced products in terms of the precision level that can be achieved in producing further products. This enhancement of the operational conditions for precision tool machining increases the level of precision for a wider range of products, reaching a higher peak for these precise products.

### 9.2 Major Findings and Original Contributions

I. The chemical composition of the thermosetting resin binder has been optimized, since it is the backbone of a PC composite. Extensive thermal, mechanical and rheological studies were carried out, as detailed in Chapter 4. The optimum resin binder composition is nominated as 40% /60% ARAPOL/MMA. It has the highest damping factor (4.5%) of all the investigated resins. The highest flexural strength is reached using the optimum resin with 128 MPa and a low strain of 10.4. It also has the highest tensile strength. The optimum resin achieves the second lowest CTE of (7.98 ×10^{-5}°C^{-1}). The nominated resin also has a low rate of viscosity increase and low temperature profile during curing. The rheological properties of the optimum resin may also enhance the mixing of the aggregate with the resin by giving more time prior to gelation, when the polymerizing mixture is still a flowing liquid. This is the fundamental contribution that laid the groundwork for further investigations of the composition of the filler, as detailed in Chapter 5. The developed polymeric binder has met the research object put forward in section 1.6.
II. The most challenging stage in the study was to nominate and validate the optimum filler composition according to the optimization criteria of the application. Some new and unique compositions were investigated for the first time, such as basalt, spodumene and fly ash and gravel, spodumene and fly ash. The optimum composition is basalt, sand and fly ash (87% filler and 13% resin), which has the lowest CTE and acceptable flexural strength considering the structural load of the application. A reduction in resin of 4% from 17% down to 13% reduces the PC damping ratio by approximately 40%. This reduction in damping ratio can be dealt with and substituted by the structural solution of increasing the damping ratio of the base. This could be achieved by attaching a single or multiple mechanical dampers in suitable positions on the PC base. The optimum filler composition is extremely cost effective compared to other comparable compositions. Through the validation of the optimum composition using FEA, the variations in deformation of the rail base were reduced to a sufficiently low level that they could be ignored. The optimized PC’s properties and its functionalities are not offered by existing feedstock materials. The optimal composition of PC, in terms of resin and composite material, has been determined on the basis of the potential use by the industrial partner. Details of this were outlined in Chapter 5. The optimum composition has met the research objectives.
III. Aspects of moulding technology have been examined individually as part of the process optimization. Each one has a different effect and influences the mechanical properties and curing behaviour of PC by various means. The optimum vibration frequency for the operation of a vibration table for the preparation of a PC sample was identified as 18.9375 Hz. An empirical relationship correlating the moulding temperature and the DMA amount was obtained. An increased DMA fraction in the resin binder has a negative impact on the mechanical properties and increases the curing rate as well as the temperature profile. Various mixing technologies were investigated for the purpose of obtaining one that could produce a PC with the highest flexural strength. It was found that MT1 is the mixing technology that can produce a PC sample with a flexural strength of 22.53 MPa, which is the maximum flexural strength compared to the others. Details were outlined in Chapter 6. This finding has met the research objective in terms of developing the moulding technology and other related aspects.

IV. Extensive experiments were carried out to fully characterize the effect of moisture on the thermal, mechanical and curing behaviour of the polymeric matrix and PC composite material. An increase in the moisture causes an increase in the curing time and hence reduces the curing rate rapidly. The effects of moisture on the mechanical properties of the resin domain (flexural strength, tensile strength, modulus of elasticity and hardness) are large and clearly apparent. An increase in moisture decreases the mechanical strength of the resin domain because of the morphological change caused by the increase in voids and micro-cracks. The DMA results emphasize the increase in the damping factor when there is an increase in the moisture content of the resin domain. The CTE of the polymeric matrix increases as the water content
increases. The influence of moisture on the main mechanical properties of the PC composite system has been revealed. An increase in moisture leads to a decrease in both the flexural and compressive strength at different rates. The CTE of the polymer concrete composite strength increases up to 50% as moisture content reaches 5%. FTIR spectroscopy scans show an interaction between water and the functional groups of the resins. Increasing the water content increases the level of non-interactive water (bulk water). When 1% of water is added to the resin composition, the share of MMA solubility (1.2 ×60%) is 0.72% and the share of Dimethyl aniline (DMA)(1.5%×0.02%) is 0.03%, and these components are soluble, as shown in Table 7.1. The total soluble water is 0.75%. In another words, the resin will reach saturation when the water added is 0.75% of the resin volume and the rest in bulk water, since the resins reach saturation when the water content is approximately 0.75%. The existence of water in the particulate fillers can have a catastrophic effect on both the productivity of a polymer concrete structure and the end-use mechanical properties. Drying of aggregate fillers which are affected by moisture should be an essential procedure for raw material preparation, and the allowable moisture must be as close to zero as possible. 0.002% would be an acceptable level of moisture in the aggregates used in the manufacture of PC composite material. Details were outlined in Chapter 7. The results presented in this chapter meet the objectives of the research in terms of identification of acceptable moisture content for the fillers, based on the influence of moisture on the thermo-mechanical properties of both composite and matrix.

V. Finally, a maturity study has been successfully conducted for PC used in the bases of precision tool machinery, for the purpose of increasing productivity and reducing the curing time. An empirical mathematical expression to
predict the correlation of the relative flexural strength with temperature as well as time of curing has been developed. Datum temperature was calculated using a mathematical model developed empirically. By increasing the temperature from 5 °C to 50 °C, the time required for curing decreased 157.65 times. Adapting the curing process in the production of a base could reduce the lead-time and enhance the quality. The existence of water in the resin diminishes the mechanical properties as the maturing temperature increases. The outcome of Chapter 8 has met the research objective in terms of developing a customized maturity method that relates to the PC base for a precision tool machine.

9.3 Recommendation and Future Work

PC has low thermal conductivity, which affects its thermal, mechanical and curing behaviour. Increasing the thermal conductivity has the potential to enhance the thermal, mechanical and curing behaviour of the PC. Emerging technologies enable the production of inexpensive and affordable nano-fibres, nano-particles and micro-particles, and the development of nano-composites offers a potential new generation of PC material that can be used for the bases of precision tool machinery. For example:

- Carbon graphite could offer a very affordable option, as could the utilisation of fillers such as silica fume fiber glass, fiber carbon and fiber polypropylene. However, certain challenges continue to hamper the development of such materials and therefore more rigorous research is required for an optimized thermal conductivity level.
These choices include nano-carbon fibres, nano-carbon tubes, micro-carbon and commercial graphite, all of which can be combined with a particular design modification of the base to achieve multi-encasements for the base. These base design modifications include the implementation of conformal cooling channels in multi-layers, which would enable the base to be further improved in terms of CTE with the enhancement of temperature distribution.

The attachment of mechanical dampers could induce an improvement of in the overall structural damping ratio of precision tool machinery. These are exemplary candidates for the development of new, higher thermal conductivity, lower CTE and higher flexural strength nano-composites or micro-composite PCs for use in the bases of precision tool machinery.

The time-dependant behaviour of polymer concrete, based on polyester resin, also influences the behaviour of precision machine bases. Properties such as the creep and shrinkage of PC bases and how these affect the stability of the application should be investigated in future research.

Further research is required in respect of the compaction of PC, considering the resin rheological, mechanical properties of the PC and the filler composition. In addition the uniformity of the PC mixture should be measured for future research.

In Chapter 7, the focus was on the moisture contents of fillers. Water absorption of aggregates is another aspect that can be recommended for future research.
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