



**Cape Peninsula  
University of Technology**

**THE INFLUENCE OF POWDER LIQUID RATIO ON THE FLEXURAL  
STRENGTH OF FIBRE REINFORCED ACRYLIC RESIN MATERIAL**

**by**

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## DECLARATION

I, Marlene du Rand, declare that the contents of this thesis represent my own unaided work, and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.



25.03.2008

Signed

Date

## ABSTRACT

Practitioners often modify the powder:liquid ratio of polymethyl methacrylate resins (PMMA) to improve the handling properties of the material for certain procedures or because of personal preferences. While it is known that this influences the mechanical properties of unreinforced resin materials, little is known about its effect on glass fibre reinforced PMMA resin.

The purpose of this study was to determine how the flexural strength of a glass-fibre reinforced PMMA provisional fixed partial denture material, is influenced by changing the powder:liquid ratio. Two main groups, each with three subgroups (n=20) was prepared for the 3-point-bending test. The first main group was unreinforced and the second main group was reinforced with glass-fibre. Each subgroup of both main groups had a different powder:liquid ratio with one of these ratios being the manufacturers recommendation and served as a control. Using a universal testing machine, maximum force in Newton (N) was determined and the flexural strength in  $\text{Nmm}^2$  was calculated using the formula:

$$\text{Flexural strength} = \frac{3F_{\max} l}{2bh^2}$$

Where

$F_{\max}$  = maximum load before fracture

l = distance between supports

b = width of specimen

h = height of specimen

Median flexural strength values were compared by means of non-parametric analysis of variance. Results were compared using the Kruskal-Wallis test. A p-value of less than 0.05 was considered significant.

The results showed that the reinforced group's median flexural strength values were significantly higher than the unreinforced group. Within the unreinforced subgroups the differences between flexural strength values were insignificant. Within the

reinforced group there was a significant difference between the control with a higher median flexural strength value than the other two ratios.

From these results it can be concluded that it is important to use the recommended powder: liquid ratio for PMMA in order to achieve maximum benefit from the glass fibre reinforcement.

**Keywords:**

Powder: liquid ratio

Flexural strength

Fibre reinforcement

Glass fibre

Polymethyl methacrylate

Provisional fixed partial dentures

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## **DEDICATION**

I dedicate this study to my family.

## TABLE OF CONTENTS

<b>Declaration</b>	<b>ii</b>
<b>Abstract</b>	<b>iii</b>
<b>Key words</b>	<b>iv</b>
<b>Acknowledgements</b>	<b>v</b>
<b>Dedication</b>	<b>vi</b>
<b>Table of contents</b>	<b>vii</b>
<b>List of figures</b>	<b>ix</b>
<b>List of tables</b>	<b>xi</b>
<b>Abbreviations</b>	<b>xii</b>

### CHAPTER ONE: INTRODUCTION

<b>1.1 Introduction</b>	<b>1</b>
<b>1.2 Statement of the problem</b>	<b>2</b>
<b>1.3 Purpose of this study and hypothesis</b>	<b>2</b>
<b>1.4 Literature review</b>	<b>2</b>
<b>a. Autopolymerising polymethyl methacrylate resin</b>	
<b>b. Powder liquid ratio</b>	
<b>c. Fibre reinforcement</b>	
<b>d. Flexural strength</b>	
<b>e. Stress-strain graphs</b>	

### CHAPTER TWO: EXPERIMENTAL DESIGN

<b>2.1 Introduction</b>	<b>10</b>
<b>2.2 Preparation of specimens</b>	<b>11</b>
<b>2.3 Testing of specimens</b>	<b>15</b>
<b>2.4 Statistical analysis</b>	<b>16</b>
<b>2.5 Fracture patterns of reinforced groups</b>	
<b>2.5.1 Macroscopic examination</b>	<b>17</b>
<b>2.5.2 Scanning electron microscopic examination</b>	<b>18</b>

<b>CHAPTER THREE: RESULTS</b>	
3.1 Introduction	19
3.2 Statistical results	19
3.3 Macroscopic fracture patterns	23
3.4 Stress-strain graphs	25
3.5 Microscopic investigation	
3.5.1 Fracture surface of the PMMA matrix	28
3.5.2 Fracture surfaces of the fibre reinforced specimens	30
<b>CHAPTER FOUR: DISCUSSION</b>	<b>34</b>
Limitations of the study	39
Possible further studies	40
<b>CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS</b>	
5.1 Summary and recommendations	41
5.2 Conclusion	42
<b>REFERENCES</b>	<b>43</b>
<b>APPENDICES</b>	<b>46</b>



## LIST OF FIGURES

<b>Figure 1:</b> Typical stress and strain graph obtained from a simple compressive or tensile test	8
<b>Figure 2:</b> Six different types of stress-strain graphs	9
<b>Figure 3:</b> Pre- impregnated ever Stick® Fibre	11
<b>Figure 4:</b> Diagram of the specimen	12
<b>Figure 5:</b> Image of the specimen	14
<b>Figure 6:</b> Stainless steel template	14
<b>Figure 7:</b> Specimen during testing	16
<b>Figure 8:</b> Schematic drawings illustrating the 4 types of fracture	17
<b>Figure 9:</b> Side-by-side violin plot demonstrating the difference in flexural strength of group A and B, and the different powder: liquid ratios within each group	20
<b>Figure 10:</b> Side-by-side box-and-whisker plots for the six experimental groups	21
<b>Figure 11:</b> Summary diagram of the Tukey-Kramer multiple-comparison test of the mean flexural strength values in Mpa.	22
<b>Figure 12:</b> A specimen from group A with type 1 fracture	23
<b>Figure 13:</b> A specimen from subgroup B1/1.5	23
<b>Figure 14:</b> A specimen with a combination fracture of type 1 and 3	24
<b>Figure 15:</b> A specimen with a combination of all four fracture patterns	24

<b>Figure 16:</b> Stress-strain graph for subgroup A 1/1	26
<b>Figure 17:</b> Stress-strain graph for subgroup A 1/0.6	26
<b>Figure 18:</b> Stress-strain graph for subgroup A 1/1.5	26
<b>Figure 19:</b> Stress-strain graph of subgroup B 1/1	27
<b>Figure 20:</b> Stress-strain graph of subgroup B 1/0.6	27
<b>Figure 21:</b> Stress-strain graph of subgroup B 1/1.5	28
<b>Figure 22:</b> SEM image of the fracture surface of the PMMA matrix of A 1/1 (x153 magnification)	29
<b>Figure 23:</b> SEM image of the fracture surface of the PMMA matrix of A 1/1.5 (x153 magnification)	29
<b>Figure 24:</b> SEM image of the fracture surface of the PMMA matrix of A 1/0.6 (x153 magnification)	29
<b>Figure 25:</b> SEM image of the pre- impregnated light-cured fibre bundle (x50 magnification)	30
<b>Figure 26:</b> SEM image of BIS-GMA fractures away from fibres (x169 magnification)	31
<b>Figure 27:</b> SEM image of the surface of fibre in specimen (x1700 magnification)	32
<b>Figure 28:</b> SEM image of fractured fibres within the PMMA matrix (x300 magnification)	33
<b>Figure 29:</b> Stress strain graph of a specimen from subgroup A 1/1	37
<b>Figure 30:</b> Stress strain graph of a specimen from subgroup B 1/0.6	38

## LIST OF TABLES

<b>Table 1:</b> Design of the study groups with different P/L ratios	10
<b>Table 2:</b> Descriptive statistics of flexural strength (MPa)	19

## ABBREVIATIONS

<b>FPD</b>	- fixed partial dentures
<b>FS</b>	- flexural strength
<b>Mpa</b>	- Mega pascal
<b>PMMA</b>	- polymethyl methacrylate
<b>P/L</b>	- powder: liquid
<b>SEM</b>	- scanning electron microscopy

# CHAPTER ONE

## INTRODUCTION

### 1.1 Introduction

Provisional fixed partial dentures (FPD) are an important aspect of successful crown and bridgework. According to Hamza et al. (2004) a provisional FPD should provide both pulpal and periodontal protection, have good marginal integrity, good aesthetics and sufficient durability to withstand forces of mastication. Autopolymerising polymethyl methacrylate (PMMA) resins are often used for directly or indirectly made provisional FPDs. However, these materials are prone to fracture under masticatory load. Masticatory forces could be high, especially in the case of long span FPDs or in patients with parafunctional habits. Also, some of the FPDs need to function in the mouth over an extended period of time. In these instances, it might be advantageous to reinforce materials.

A number of different techniques for reinforcing PMMA resin have been suggested. Metal wire strengtheners and mesh have often been used as reinforcements. However, the bond between the metal and the PMMA matrix proved insufficient (Vallittu, 1993).

The introduction of fibres addressed this lack of bond between metal and PMMA. Manufacturers of different types of fibres claim improved reinforcement properties of fibres due to a chemical adhesion between the fibres and the PMMA matrix (Vallittu, 1998). Comparing the different types of fibres, glass fibres seem to show the best results in this regard (Hamza et al., 2004).

Autopolymerising PMMA resins are often presented as powder liquid (P/L) combinations that need to be mixed in order to start the polymerisation process. Powder liquid ratios are sometimes modified in order to change the handling properties of the mixture. Williams et al. (2001) found that this habit may have deleterious effects on the properties of the polymerised material. Syme et al. (2001) found that while the stiffness of autopolymerising resins

was unaffected by variations in P/L mixing ratio, extension to failure was greater with lower P/L ratios. Little research has been done on the effect of different P/L ratios on the adhesion of the PMMA mixture to the glass fibre bundle.

## **1.2 Statement of the problem**

Practitioners often modify the P/L ratio of PMMA resins to improve the handling properties of the material for certain procedures or because of personal preferences. While it is known that this influences the mechanical properties of unreinforced resin materials, little is known about its effect on glass fibre reinforced PMMA resin.

## **1.3 Purpose of the study and hypothesis**

The purpose of this research is to determine how the flexural strength of a glass-fibre reinforced PMMA material for provisional FPDs is influenced by different P/L ratios by applying the 3-point bending test.

The results of this research could assist in a recommendation for the appropriate P/L ratio in order to achieve maximum benefit from the glass fibre reinforcement.

### **Hypothesis:**

A lower or a higher than the recommended P/L ratio decreases the flexural strength of glass fibre reinforced PMMA material for provisional FPDs.

## **1.4 Literature review**

### **a. Autopolymerising PMMA resin material**

Autopolymerising PMMA resin has been used for many years for provisional FPDs (Hamza et al., 2004). It has good aesthetics and it is easy to work with. However, its disadvantages are 1) exothermic polymerisation reaction, 2) toxic effect of the monomer on tissue, 3) polymerisation shrinkage and, 3) low mechanical fracture behaviour

(Lang et al., 2003). Gegauff and Pryor (1987) attribute the low fracture behaviour to the fact that these resins consist of low-molecular weight, linear molecules not capable of crosslinking with other monomer chains. In addition, they show high force deformation.

The materials are marketed as P/L combinations to be mixed according to a certain ratio, as prescribed by the manufacturer.

**b. Powder: liquid ratio**

Clinical and laboratory dental staff does not always follow the manufacturer's recommended guidelines for P/L ratios. The ratio is sometimes changed in order to achieve a certain consistency. Williams et al. (2001) found that this habit may have deleterious effects on the properties of the polymerised material.

According to Anusavice's study in 2003 the fabrication of well-fitting denture bases with desirable physical properties, the proper polymer: monomer ratio is of considerable importance. He also found that most discussions of polymer: monomer ratios are vague and provided little practical information for dental personnel.

In addition, Vallitu (1999) mentioned that a higher liquid content in the mixture increases polymerisation shrinkage in the resin. He says that this polymerisation shrinkage might cause a slit between the fibre and the polymer matrix, reducing the amount of adhesion between the two components and ultimately the strengthening effect. According to Syme et al. (2001), it was found that while the stiffness of autopolymerising resins was unaffected by variations in P/L mixing ratio, extension to failure was greater with lower P/L ratios.

**c. Fibre reinforcement**

Different methods of reinforcing PMMA resin materials have been used in the past. Currently, the reinforcement with different types of fibres is popular because of their dimension and neutral colour. Three different fibre reinforcements have been suggested: polyethylene fibres, carbon fibres or glass fibres.

In 1997, Samadzadeh et al. tested polyethylene fibres in PMMA and found that the use of this fibre was an effective method of reinforcing interim FPDs. However more, recently a study by Hamza et al. (2004) demonstrated a significant difference in the reinforcing potential of polyethylene fibres among specific brands and the types of polymers used. They mentioned the importance of using well impregnated, silanized, plasma-treated fibres to achieve good adhesion of the fibre to the polymer.

Investigations have demonstrated that carbon fibre reinforced polymers have a higher flexural strength than unreinforced polymers (Hamza et al., 2004). However, the main disadvantage of carbon fibres is its black colour and its radiolucency (Shetty et al., 2005). The colour of the carbon fibres makes it a difficult material to use where aesthetics is important.

Therefore, glass fibres have proven to be the most ideal fibre of all three. Silanized glass fibres demonstrate good adhesion to the polymer matrix, high aesthetic quality, and increased strength of the resulting composite (Hamza et al., 2004).

According to Hamza et al. (2004) the addition of fibres to provisional restorative resin material increases both fracture toughness and flexural strength. Nohrstrom et al. (2000) found that the reinforcement of interim FPDs with glass fibres is most evident with long span bridges. They also found that the location of the fibre within the FPDs is important. The positioning of the reinforcement at the tension side increases the fracture resistance more than if it was placed at the compression side of the prosthesis. These results confirm those of Vallittu (1998) who found that even though the glass fibre reinforcements were positioned on the least favourable side of the fixed partial denture, the fracture resistance was still considerably increased compared to using no fibre at all.

Another critical factor affecting the strength of fibre reinforced composites, according to Lassila et al. (2004), is the adhesion



between the fibres and the resin matrix. They say that without adequate adhesion the fibre acts as an inclusion in the resin matrix that weakens the composite.

The following paragraph is quoted from the StickTech website:  
([www.sticktech.com](http://www.sticktech.com), 2007)

*“The bonding capability of Stick and everStick to composite resin and adhesive/composite cements has been shown to be excellent.*

*The increase in bond strength can be achieved by taking advantage of the unique Interpenetrating Polymer Network structure (IPN structure) within Stick and everStick polymer matrices.*

*It is based on the ability of the polymer matrix to partially dissolve in the resin used for bonding. The PMMA pre-impregnation, used in both Stick and everStick, is performed by using a thermoplastic polymer, which is capable of dissolving into the resins used for wetting, luting and composite veneering. The surface of the fiber framework is partially dissolved with resin, resulting in a micro mechanical as well as a chemically bonded interface.”*

Lassila et al. (2004) found that the light curing process has an influence on the hardness and flexural properties of a composite resin. The higher the degree of monomer conversion, usually the better the mechanical properties.

Glass fibres come in different shapes and sizes. Woven fibres are thicker, and because of their multidirectional reinforcement of the PMMA matrix, they provide better strengthening characteristics (Vallittu, 1999). The strength of the consequential reinforced structure is dependant on the volume of the fibres embedded in the PMMA matrix and the degree of adhesion between the fibre and the polymer. The higher the number of fibres and the better the adhesion, the more improved the strengthening characteristics are (Kim and Watts, 2004).

**d. Flexural strength testing**

Flexural strength can be defined as the strength of the material in bending, expressed as the tensile stress of the outermost fibres of a bent test sample at the instant of the failure ([www.rtpcompany.com](http://www.rtpcompany.com)).

The flexural strength is the unit resistance to the maximum load before failure by bending (www.fibreglast.com, 2007).

The flexural strength of a material is a combination of compressive, tensile, and shear strengths (Jacob et al., 2001): a flexure test produces tensile stress in the convex side of the specimen and compression stress in the concave side, creating an area of shear stress along the midline. As the tensile and compressive strengths increase, the force required to fracture the material also increases. To ensure the primary failure comes from tensile or compression stress, the shear stress must be minimized. Controlling the span to depth ratio does this (Jacob et al., 2001).

Different flexural strength tests exist to quantify the failure of materials. One such a test is the 3-point bending test. In a 3-point bending test, the area of uniform stress is quite small and concentrated under the central loading point (Kanie et al., 2000).

Flexural strength can be calculated using the following equation: (Kanie et al., 2000)

$$\text{Flexural strength} = \frac{3F_{\max}l}{2bh^2}$$

Where

$F_{\max}$  = maximum load before fracture

$l$  = distance between supports

$b$  = width of specimen

$h$  = height of specimen

e. **Stress-strain graphs**

The following paragraphs on stress, strain and stress-strain relationship are adapted from McCabe (1985), except when indicated otherwise.

**Stress:** When an external force is applied to a specimen of material under test, an internal force, equal in magnitude but opposite in direction, is set up in the body. For compression or tension the stress is

given by the expression:  $\text{Stress} = F/A$  where  $F$  is the applied force and  $A$  the cross-sectional area of the specimen. A stress resisting a compressive force is referred to as a compressive stress and that resisting a tensile force a tensile stress.

**Strain:** The application of an external force to a test specimen results in a change in dimension of the specimen. For example, when a tensile force is applied the body undergoes an extension, the magnitude of which depends on the applied force and the properties of the material.

The numerical value of strain is given by the expression:

$$\text{Strain} = \frac{\text{change in length}}{\text{original length}}$$

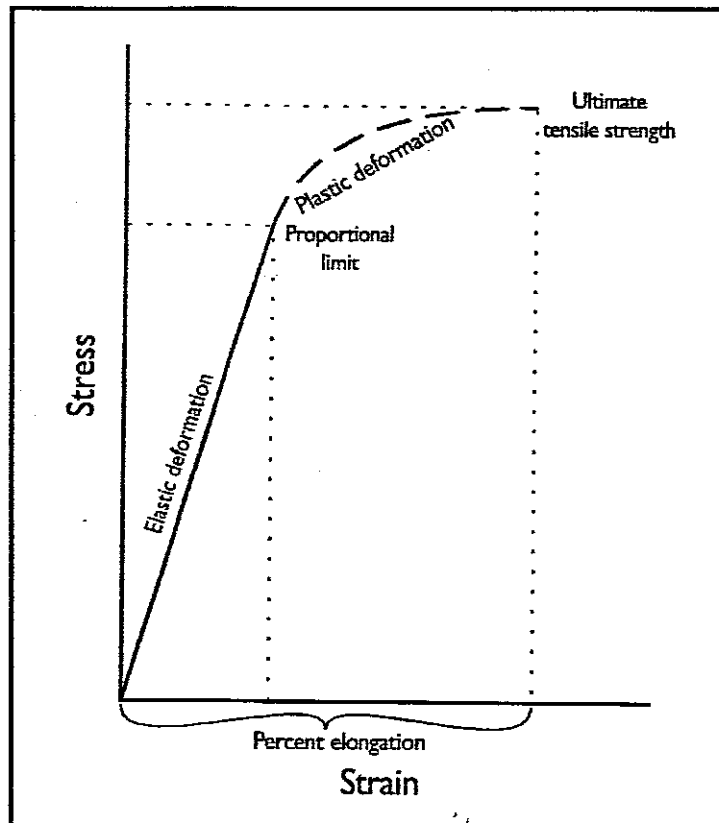
Thus strain, which has no physical dimensions, can be seen as a measure of the fractional change in length caused by an applied force.

**Stress-strain relationship:**

Stress and strain are not independent and unrelated properties, but are closely related and may be seen as an example of cause and effect.

The application of an external force, producing a stress within a material, results in a change in dimension or strain within the specimen.

Illustrated in figure 1, is the measurement of stress and strain on an object being stretched (O'Brien, 1997).



**Figure 1: Typical stress and strain graph obtained from a simple compressive or tensile test. (O'Brien, 1997)**

In the region labelled “elastic deformation”, stress is proportional to strain, whereas in the region labelled “plastic deformation”, stress and strain are no longer proportional (strain increases faster than stress does). The highest point at which stress and strain are still proportional is called the proportional limit, and the maximum stress just before the object breaks is called the ultimate tensile strength. The total amount that the object stretches (i.e., the total strain), which is the sum of the elastic deformation and the plastic deformation, is called the percent elongation. (O'Brien, 1997)

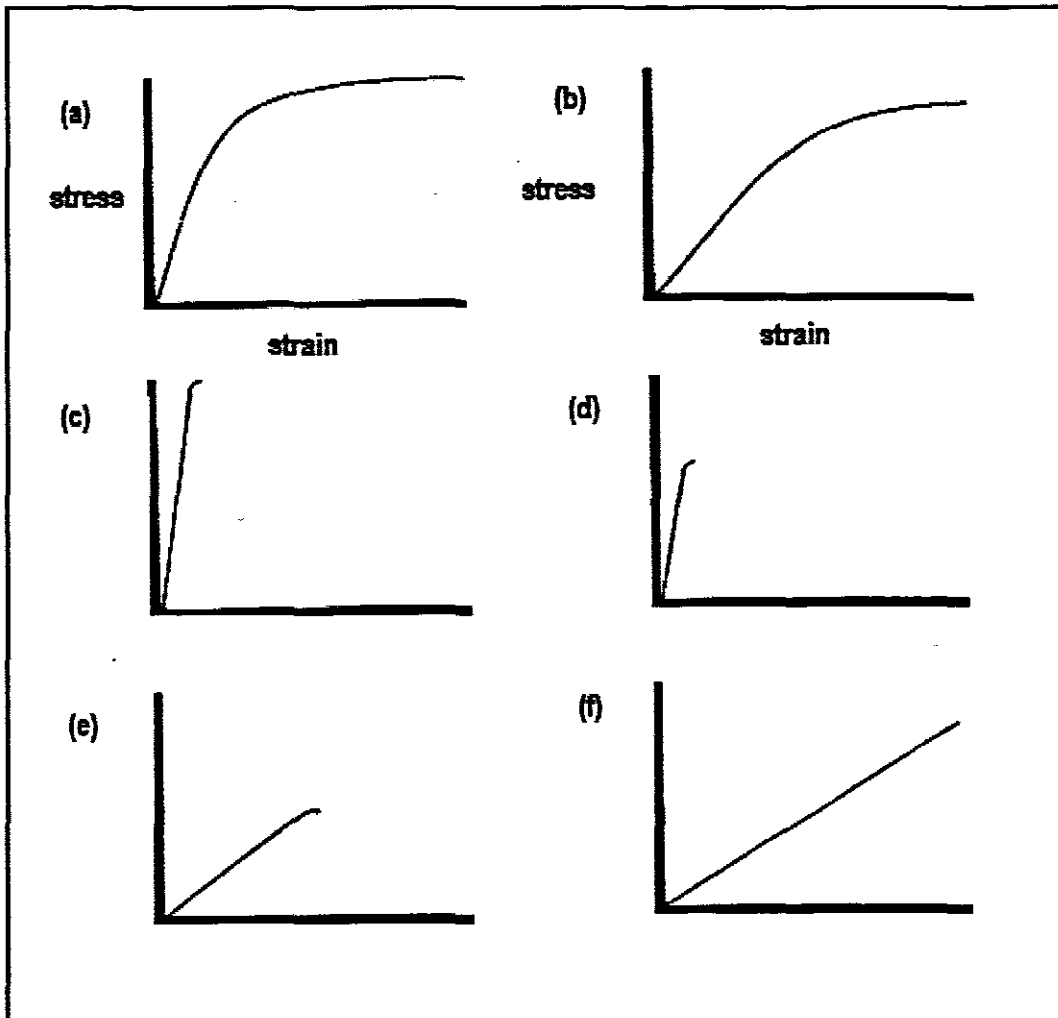


Figure 2: Six different types of stress-strain graphs. (McCabe, 1985)

The graphs in figure 2 may be used to characterise materials as follows: (a) rigid, strong, tough, ductile; (b) flexible, tough; (c) rigid, strong, brittle; (d) rigid, weak, brittle; (e) flexible, weak, brittle; (f) flexible, resilient. (McCabe, 1985)

## CHAPTER TWO

### EXPERIMENTAL DESIGN

#### 2.1 Introduction

Two test groups of SR Ivocron® (Ivoclar Vivadent AG, Schaan, Liechtenstein) provisional crown and bridge material have been prepared: group A, not reinforced, consisted of three subgroups with three different P/L ratios, and group B, reinforced, consisted of three subgroups with the same three different P/L ratios (table 1). Twenty one specimens were made for each subgroup. Pre-impregnated everStick® C&B fibre (Stick Tech, Turku, Finland) was used as the reinforcement fibre (figure 3).

The product specifications of the SR Ivocron® are represented in appendix A. One of the subgroups in group A and B used the manufacturer's recommended P/L ratio. This ratio served as the control ratio. The manufacturer's recommended P/L ratio is 1/1 in volume and 1/0.83 in weight. A pilot study was conducted to determine the two other ratios in the groups. During this pilot study it was found that the two ratios at each side of the recommended ratio were extreme ratios that could not be extended further without severely compromising ease of handling.

**Table 1: Design of the study groups with the different P/L ratios**

<b>Group A (without fibres)</b>			
<b>P/L<sup>v</sup></b>	1/1.5	1/1 (control)	1/0.6
<b>P/L<sup>g</sup></b>	1/1.245	1/0.83	1/0.498
<b>Group B (with fibres)</b>			
<b>P/L<sup>v</sup></b>	1/1.5	1/1 (control)	1/0.6
<b>P/L<sup>g</sup></b>	1/1.245	1/0.83	1/0.498

$P/L^v$  = powder liquid ratio in volume

$P/L^g$  = powder liquid ratio in weight

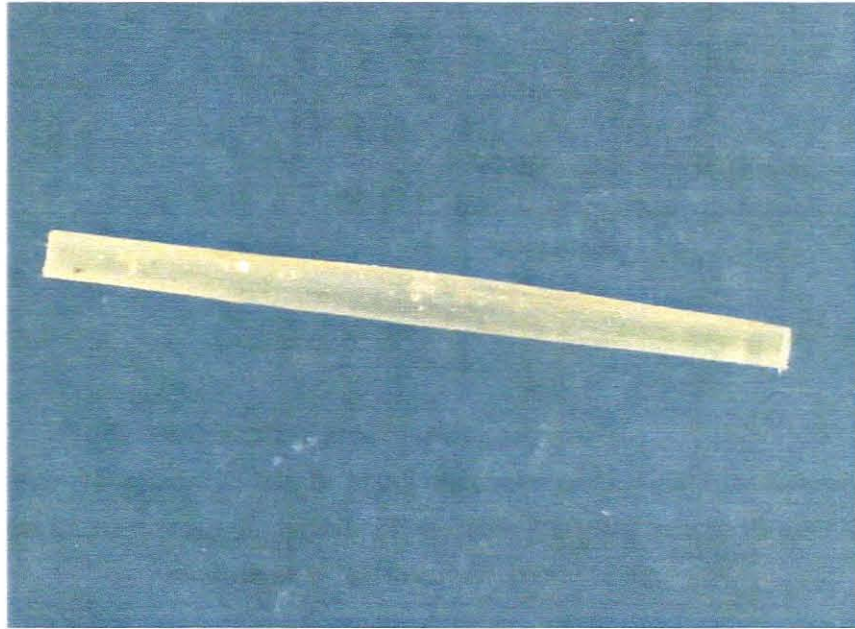
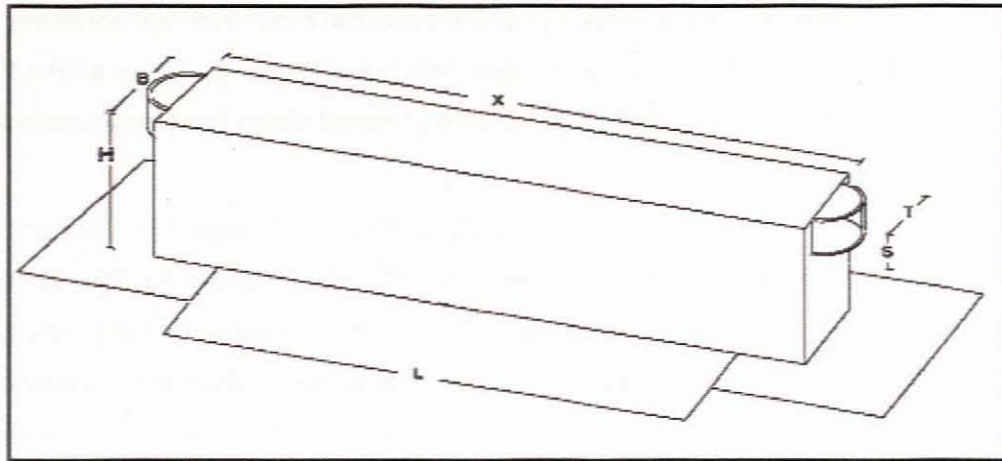


Figure 3: Pre- impregnated everStick® Fibre

## 2.2 Preparation of specimens

Each specimen was prepared for the 3-point bending test. A custom-made stainless steel template was fabricated for this purpose. The overall dimensions of the specimens were 3mm x 6mm x 25mm.



<b>B= 3mm</b>	<b>X= 25mm</b>
<b>H= 6mm</b>	<b>S= 2mm</b>
<b>L= 20mm</b>	<b>T= 1.5mm</b>

**Figure 4: Diagram of the specimen**

**B= width, H=height, X= length of the specimen and L= distance between supports of the three-point bending apparatus (drawing adapted from MChD minithesis by JH Overturf, UWC, 2006).**

The PMMA was mixed using the accurate ratios as determined by the pilot study. The mixing ratios are in gram; therefore the polymer and monomer were weighed using an analytical laboratory balance (Denver Instrument Company., Göttingen, Germany) with an accuracy of 0.0001gram. The monomer and polymer were weighed in a glass beaker using the taring option on the scale, which subtracted the glass beakers weight to get the correct weight of the material. A 2ml Pasteur pipette (Vacutest KIMA, Arzergrande, Italy) was used to ensure the correct amount was measured. The PMMA was mixed in the glass beaker, in which the monomer was weighed, to eliminate loss of liquid during transfer.

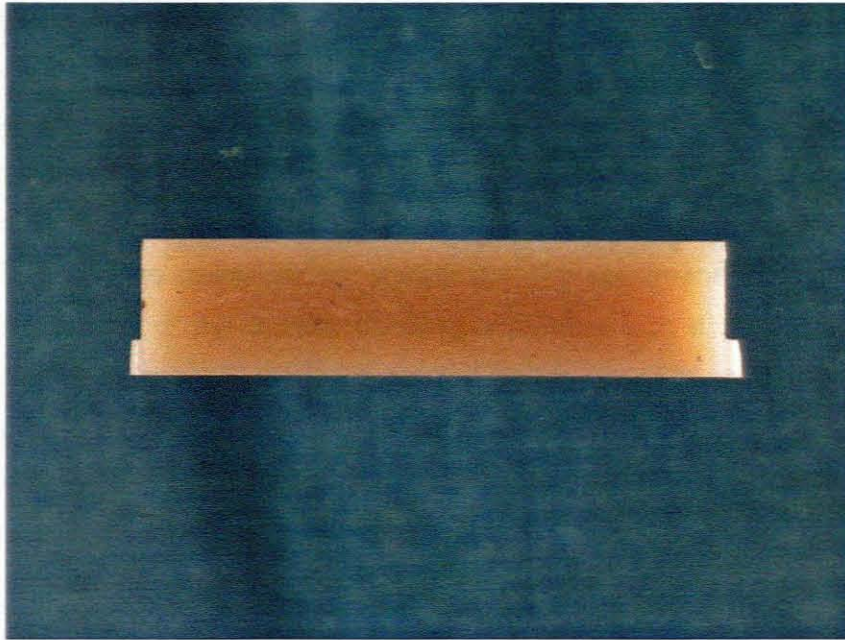
For group A no fibres were used.

For group B before mixing the monomer and polymer, the pre-impregnated fibre was prepared. This entailed the removing of the fibre from its silicone casing, cutting the fibre with a scalpel to the correct length of 27 mm and polymerising the fibre in the light cure unit (Megalight MINI, Radeburg, Germany) for 2 minutes. It was important to cut the fibre before polymerising

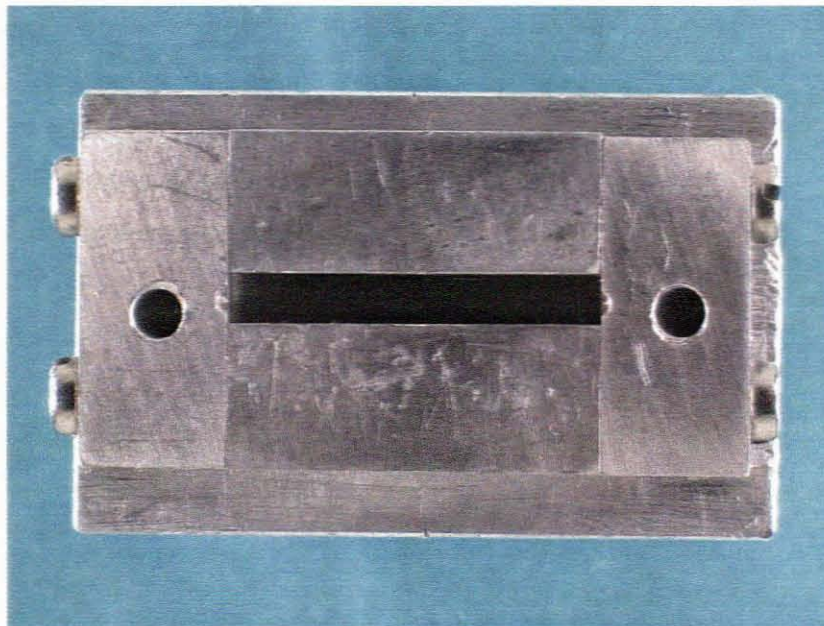


otherwise the fibre becomes too hard to cut. After 2 minutes in the curing unit, the fibre was fully polymerised and ready to be placed. Polymerising the fibre before placement made handling and timing of the procedure easier.

The template was filled with PMMA up to the height of the lateral stops on each side of the template. The polymerised fibre, cut to length, was then placed parallel to the long axis of the specimen into the unpolymerised PMMA material. The ends of the fibre rested in the lateral stops of the template. More resin was added and the template was slightly overfilled. The surface was covered with a plastic matrix strip and a thick glass plate. A pressure of 5 kg was applied during the initial first 8 minutes for 1 minute to squeeze out excess material and to minimize porosity. The template was then placed, without the weight, in the pressure pot (Palamat practice Kulzer, Homburg, Germany) following the manufacturers requirements, at 2 bar for 15 minutes submerged in 40-50°C water. After polymerisation, the template was disassembled and the specimen removed. After removal, the edges of the specimen were finished with fine grit carbide paper and the width and height of each specimen were recorded twice using a digital height gauge (Mitutoyo Corporation, Japan) with an accuracy of 0.01 mm. The averages of these measurements were used in the flexural strength formula as will be explained in paragraph 2.3.



**Figure 5: Image of the specimen**



**Figure 6: Stainless steel template**

### 2.3 Testing of specimens

The specimens were stored dry before testing using the Zwick universal testing machine (Model 1446, Zwick, Ulm, Germany). This machine is used in conjunction with the computer program TestXpert® which converts the data to be used by the statistician for analysing. The specimens were positioned on the supports of the 3-point bending apparatus with a fixed span width of 20mm. A mechanical load was applied on the centre of each specimen at 90 degrees to the specimen axis through a stainless steel rod. By movement of the crosshead, with a speed of 6mm/min, using a loading cell of 5kN, the load was increased until failure of the specimen.

The maximum strength of the specimen was recorded as  $F_{max}$ , and flexural strength was calculated using the following equation:

(Kanie et al., 2000)

$$\text{Flexural strength} = \frac{3F_{max}l}{2bh^2}$$

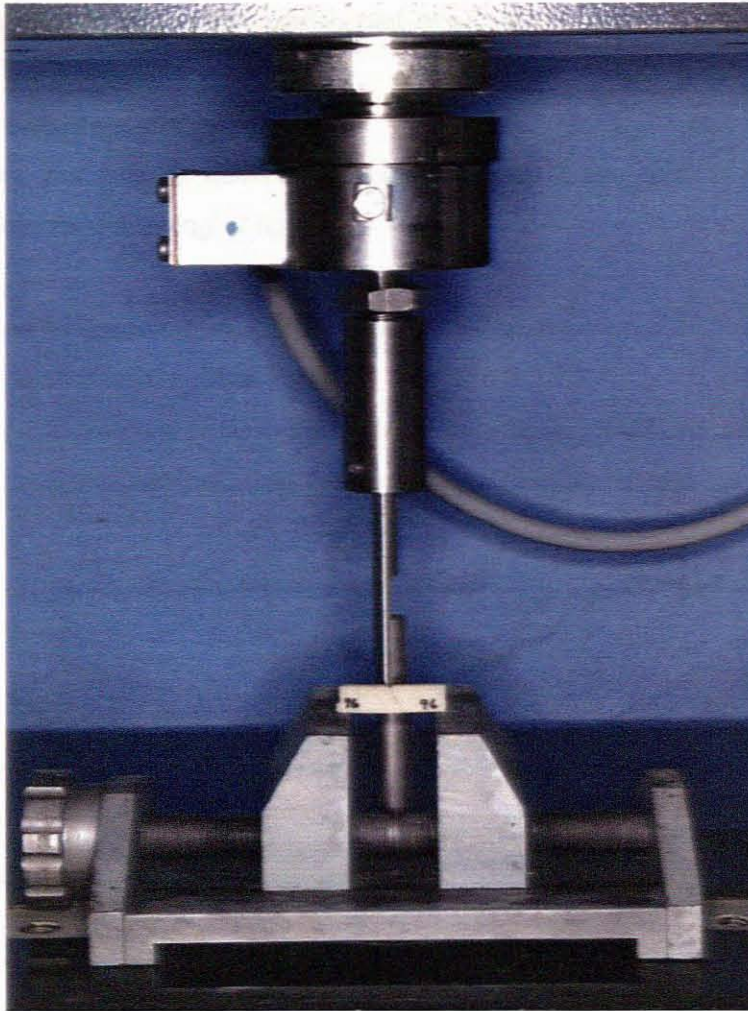
Where

$F_{max}$  = maximum load before fracture,

$l$  = distance between supports,

$b$  = width of specimen

$h$  = height of specimen



**Figure 7: Specimen during testing**

## **2.4 Statistical analysis**

The results are presented by means of descriptive statistics and analysed by means of multiple comparisons according to the Tukey-Kramer method. The subgroups with different P/L ratios within group A and B are compared with the control ratio. Between groups A and B the same ratios are compared using the Wilcoxon rank sum test. A p-value of less than 0.05 is considered significant.

## 2.5 Fracture patterns of the reinforced groups

### 2.5.1. Macroscopic examination

Fracture patterns for each sub group of group B are described according to the schematic drawing of figure 8.

1. Type 1: fracture through the PMMA matrix.
2. Type 2: fracture of the fibres.
3. Type 3: fracture between the PMMA matrix and the fibre bundle.
4. Type 4: fracture between the impregnation material and the fibre.

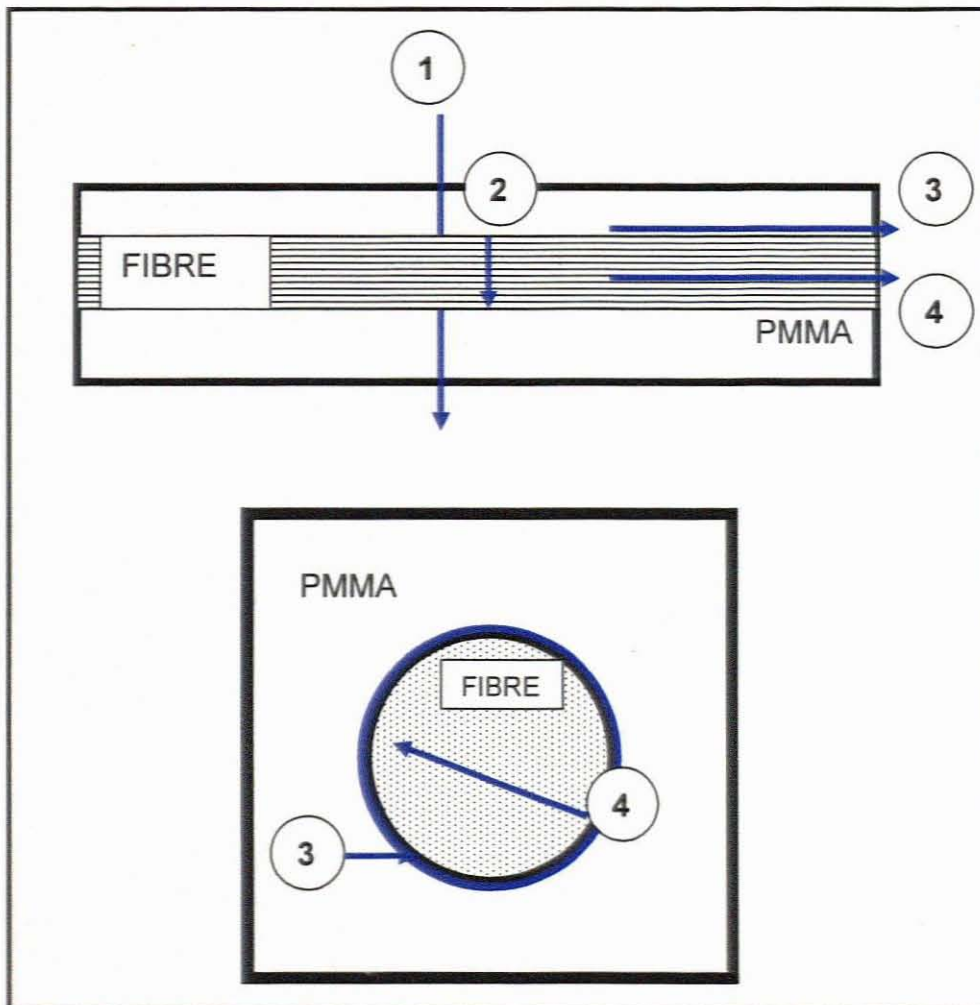


Figure 8: Schematic drawings illustrating the 4 types of fractures.

### 2.5.2. Scanning electron microscopic examination

Some of the fractured specimens of group B were examined by means of the scanning electron microanalyser (SEM) (Hitachi,model X-650,Tokyo, Japan) to gain more detail on the fracture patterns. The scanning was done at 25keV.

## CHAPTER THREE

### RESULTS

#### 3.1 Introduction

The flexural strength values in Mpa for the 3 different P/L ratios within groups A and B will be presented. The results following comparison of the flexural strength of the 3 different P/L ratios within groups A and B will be presented using box-and-whisker and violin plots.

One specimen from group A ratio 1/1 and one specimen from group B ratio 1/0.6 were not included in the analysis of the results, because of test failure: movement of the specimen on the supports was observed during loading before failure.

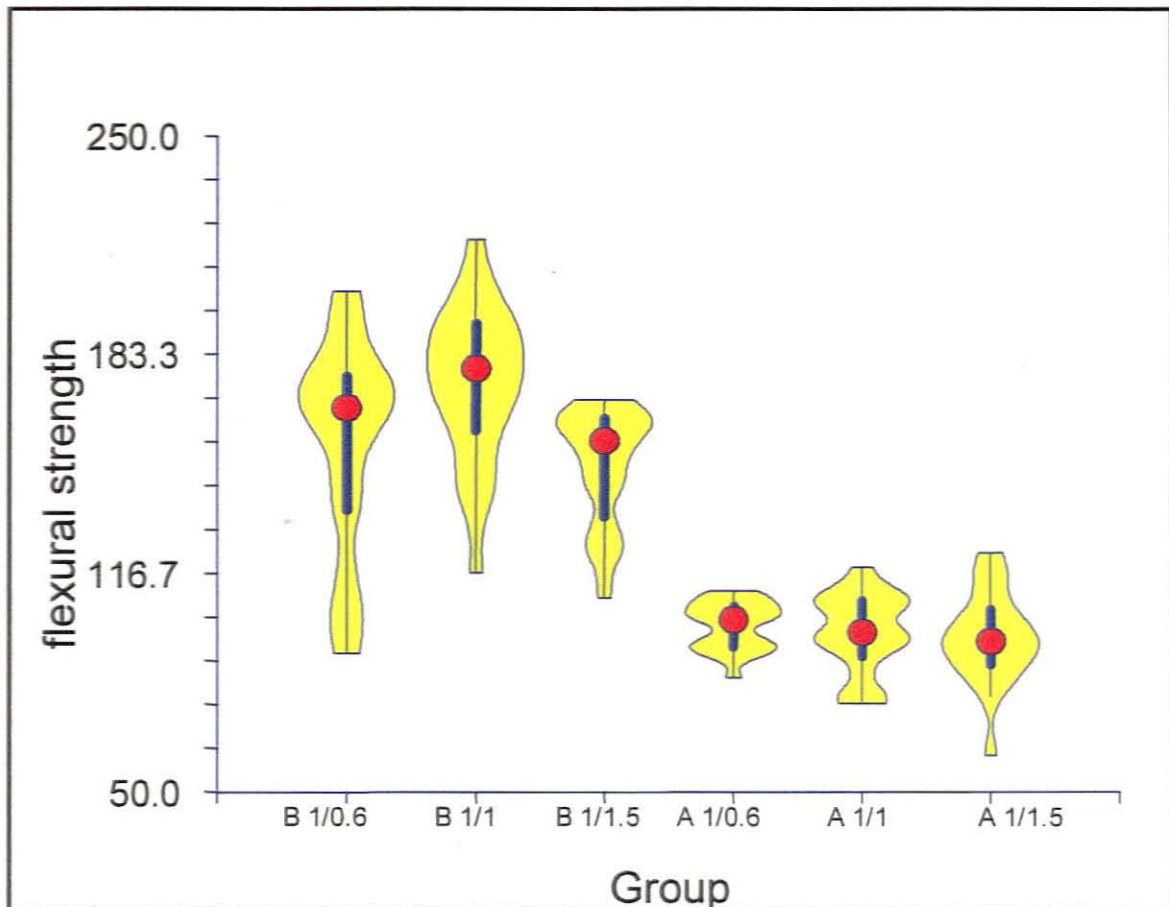
#### 3.2 Statistical results

The flexural strength values of all groups are presented in table 2.

All the subgroups in group B (with fibres) have a significantly higher flexural strength than the specimens in group A (without fibres). There is no overlapping of the mean values between the groups A and B. The subgroup in group B with the lowest average flexural strength (1/1.5) is still higher than the subgroup in A with the highest flexural strength (1/0.6).

**Table 2: Descriptive statistics of flexural strength (Mpa). Subgroup B 1/1 has the highest mean (174.35) of all subgroups; subgroup A1/1.5 has the lowest mean (96.99)**

Ratio	Group A			Group B		
	1/0.6	1/1	1/1.5	1/0.6	1/1	1/1.5
<b>Count</b>	21	20	21	20	21	21
<b>Mean</b>	100.63	98.56	96.99	156.34	174.35	149.10
<b>Median</b>	102.7	98.8	96.1	166.9	179.0	156.9
<b>Std Deviation</b>	7.34	12.11	14.16	32.67	24.13	17.90
<b>Minimum</b>	84.96	76.92	61.34	92.29	116.88	109.13
<b>Maximum</b>	111.42	118.52	122.92	202.51	218.23	169.44

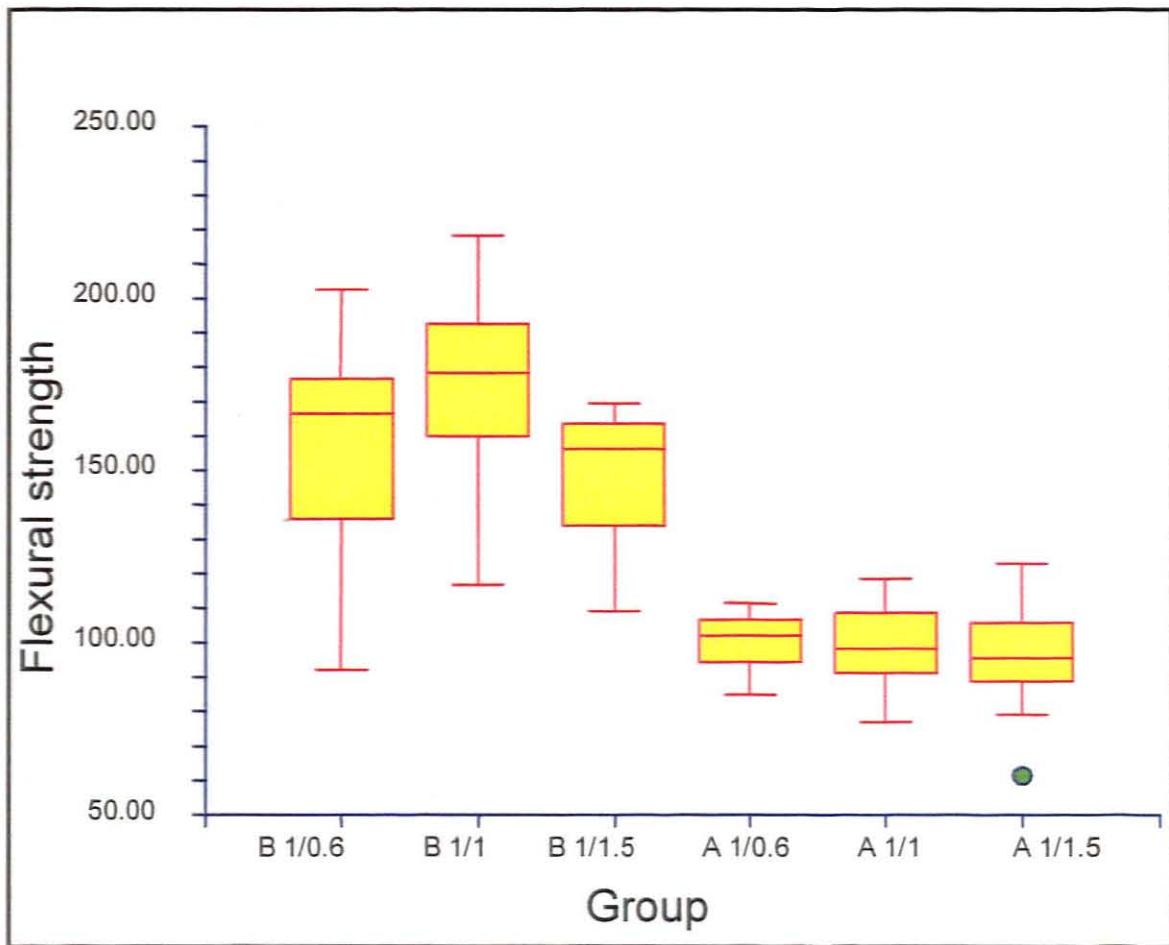


**Figure 9: Side-by-side violin plot demonstrating the difference in flexural strength of group A and B, and the different P/L ratios within each group.**

The violin plot is a density estimate, the smaller the width the less observations in those intervals. The red dot towards the middle of the violin plot represents the median and the thick blue vertical bar links the first quartile to the third quartile. The thick blue vertical bar passes through the median (the second quartile).

The three subgroups reinforced with fibres have a significantly higher flexural strength than the three subgroups without fibres. Within the two groups there are hardly any differences between the medians. The distributions of subgroups B 1/0.6, B 1/1 and B 1/1.5 display heavy tails for smaller flexural strengths. The three mixes within group A have approximate symmetrical distributions.







**Figure 10: Side-by-side box-and-whisker plots for the six experimental groups.**

The box-and-whisker plot is more robust than the violin plot and provides an indication of the minimum, first quartile, median, third quartile and the maximum. If outlying observations are present it is indicated by means of a green dot as can be seen in group A 1/1.5. The value of this outlier was 61.34. The same deductions can be made as with the side-by-side violin plots.

The multiple comparisons findings according to the Tukey-Kramer method are summarised in figure 11. Those groups linked by means of a black line, do not differ statistically ( $p$  value  $> 0.05$ ).

	Group A			Group B		
Ratio	1/1.5	1/1	1/0.6	1/1.5	1/0.6	1/1
Mean	96.99	98.56	100.63	149.10	156.34	174.35
						

**Figure 11: Summary diagram of the Tukey-Kramer multiple-comparison test of the mean flexural strength values in Mpa.**

In group A there is no significant difference in the flexural strength within the three different P/L ratios.

In group B, there is no significant difference between the ratios of 1/1.5 and ratio 1/0.6, but there is a significant difference between these two ratios and the recommended ratio of 1/1.

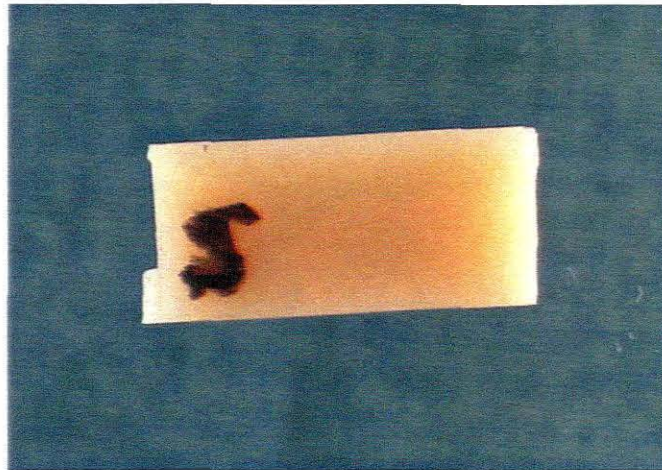
The same P/L ratios between group A and B, for example A 1/1.5 compared with B 1/1.5, were also analysed.

For the 1/1 ratio, the flexural strength of group B was 77% higher than group A. For the 1/1.5 ratio, the flexural strength of group B was 54% higher than group A.

For the 1/0.6 ratio, the flexural strength of group B was 55% higher than group A.

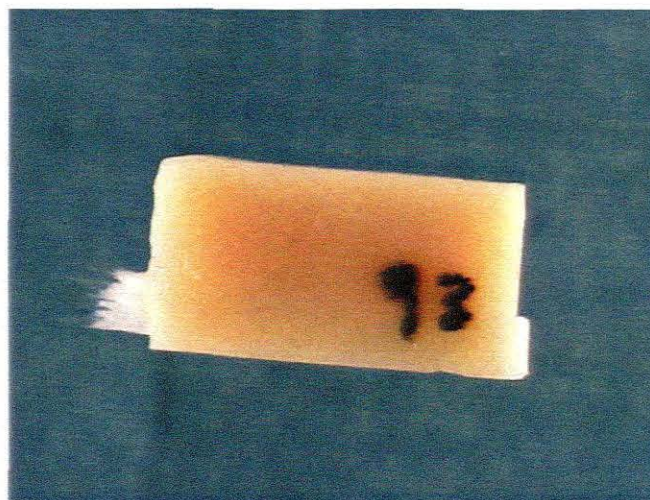
### 3.3 Macroscopic fracture patterns

All specimens from group A showed the same fracture pattern: type 1 (Figure 12)



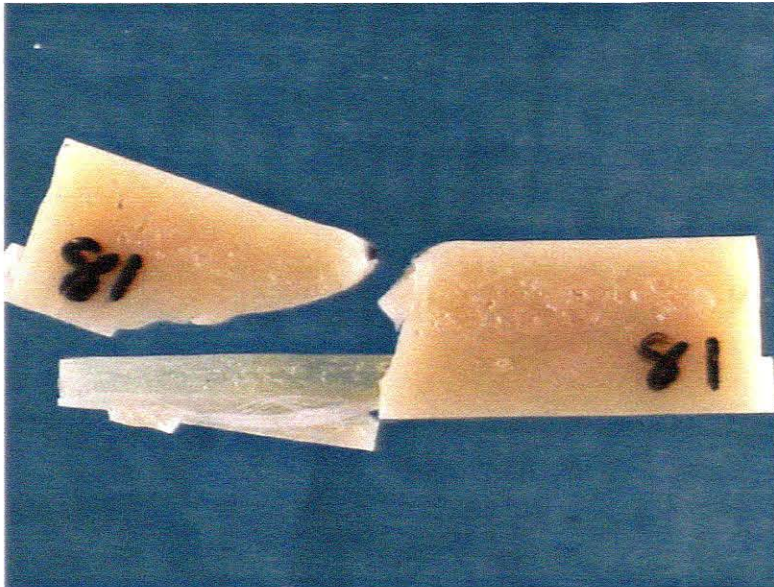
**Figure 12: A specimen from group A with type 1 fracture.**

In group B the fracture patterns differed from group A. In subgroup B 1/1.5, the dominant fracture pattern was in the PMMA matrix parallel to the load and the fibre bundle fractured according to a type 2 fracture pattern. (Figure 13)

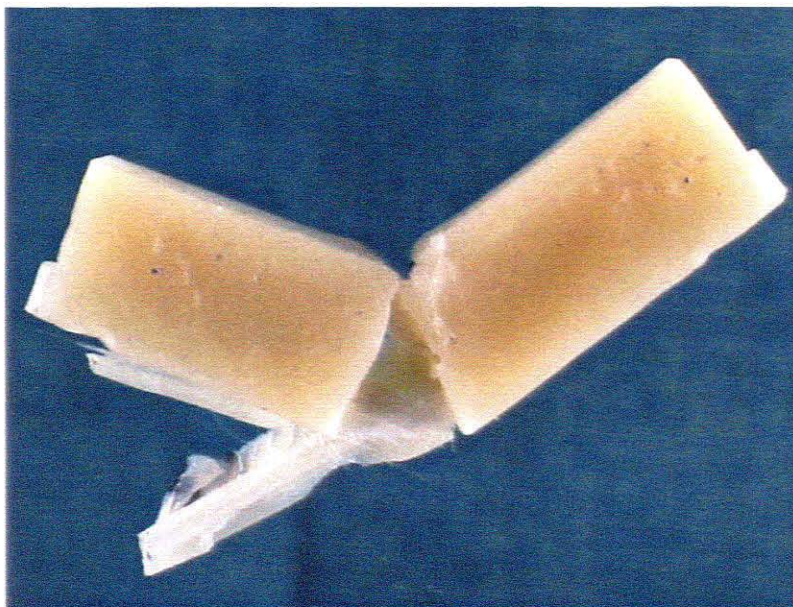


**Figure 13: A specimen from subgroup B1/1.5**

For subgroups B 1/1 and B 1/0.6, a type 1 fracture in combination with predominantly type 3, but also type 4 fractures were observed. (Figure 14 and 15)



**Figure 14: A specimen with a combination fracture of type 1 and 3.**

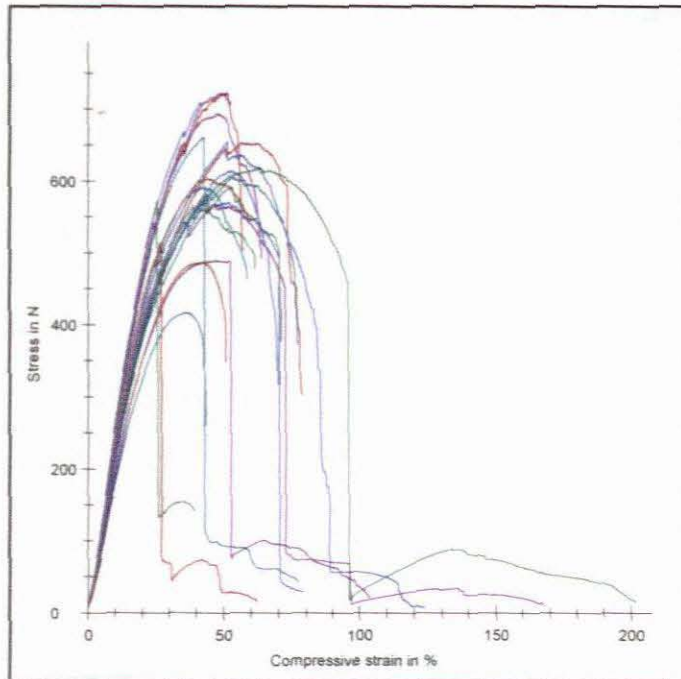


**Figure 15: A specimen with a combination of all four fracture types.**

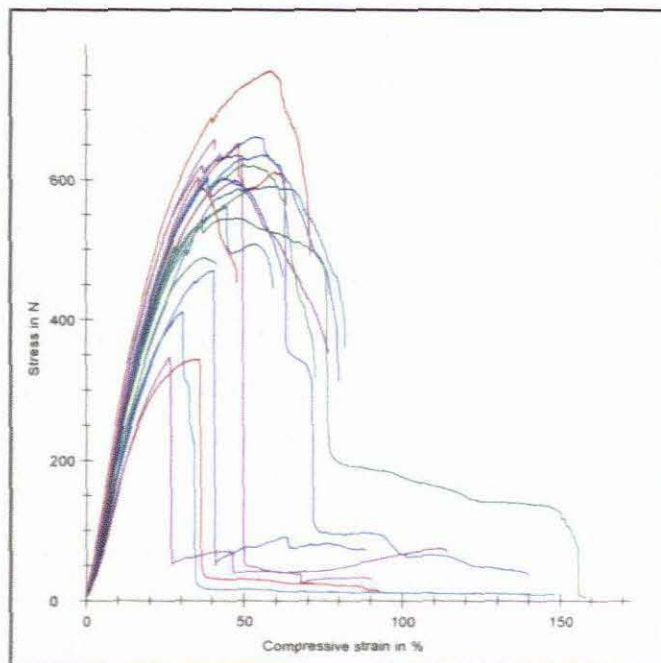
### **3.4 Stress-strain graphs**

Figures 16, 17 and 18 show the stress strain graph of the three subgroups of group A. The graphs for A 1/1 and A 1/0.6 are very similar, but A 1/1.5, the more fluid mixture, shows more plastic deformation towards the end of the graph.

Figures 19, 20 and 21 demonstrate the stress-strain graphs for the three subgroups of group B. Figures 19 and 20 look similar and represent subgroups B 1/0.6 and B 1/1. Both these ratios specimens' stress and strain graphs reflect combination fractures.



**Figure 19: Stress-strain graph of subgroup B 1/1.**



**Figure 20: Stress-strain graph of subgroup B 1/0.6.**

For subgroup B 1/1.5, the most liquid mixture of group B, the type 1 fracture in combination with type 2 was the most dominant fracture pattern. For all specimens except one, the stress-strain graphs indeed show a sudden fracture and an end of the test when the specimens fracture in two pieces.

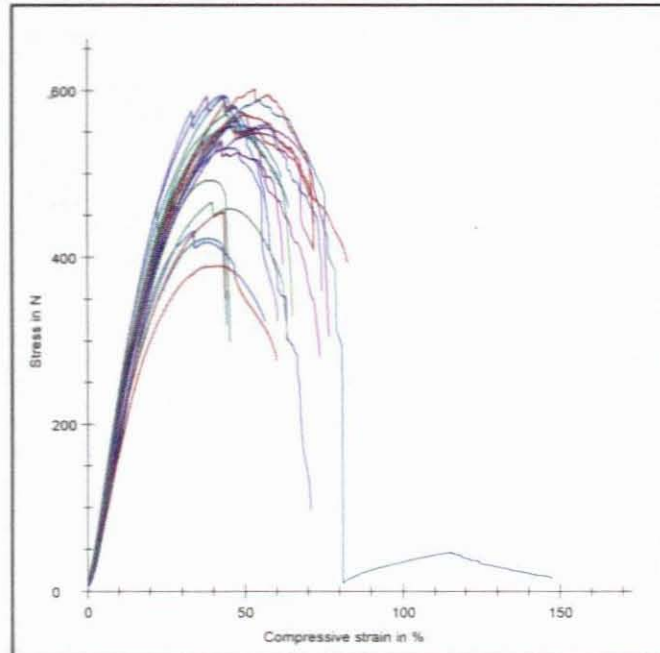


Figure 21: Stress-strain graph of subgroup B 1/1.5

### 3.5 Microscopic investigation

Representative specimens from different groups were prepared to be viewed under SEM.

#### 3.5.1. Fracture surface of the PMMA matrix.

An SEM investigation of the specimens' fracture surfaces demonstrates a different grain structure for each P/L ratio. Figures 22, 23 and, 24 show the fracture surfaces of the PMMA matrix of the three different ratios under x153 magnification.

The fracture surface of the 1/0.6 ratio is rougher than the fracture surface of the 1/1.5 mixture, which has a finer grain structure.

The fracture surface of the 1/1 mixture (control) indicates a grain structure in between the rough 1/0.6 and the fine 1/1.5 grain structure.

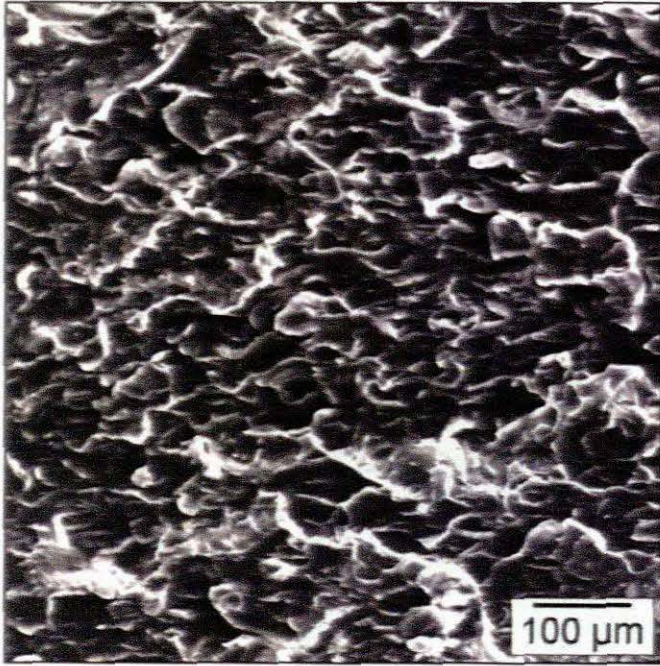


Figure 22: A 1/1

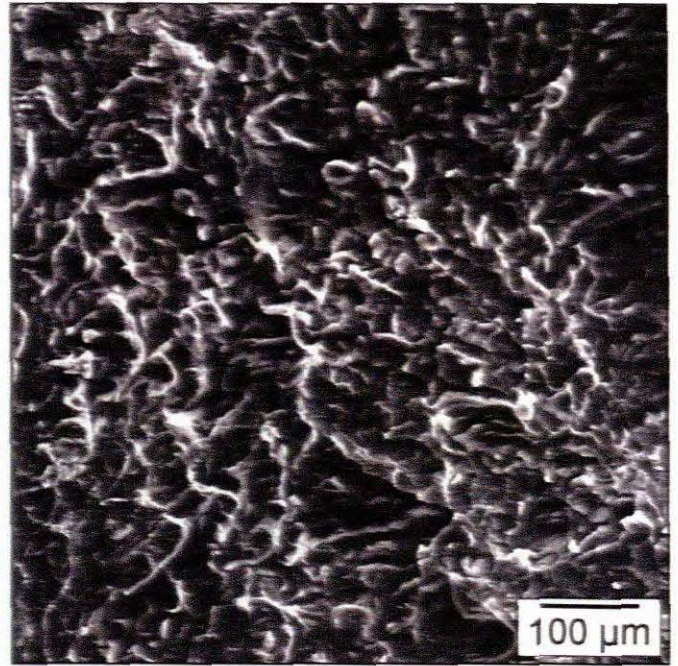


Figure 23: A 1/1.5

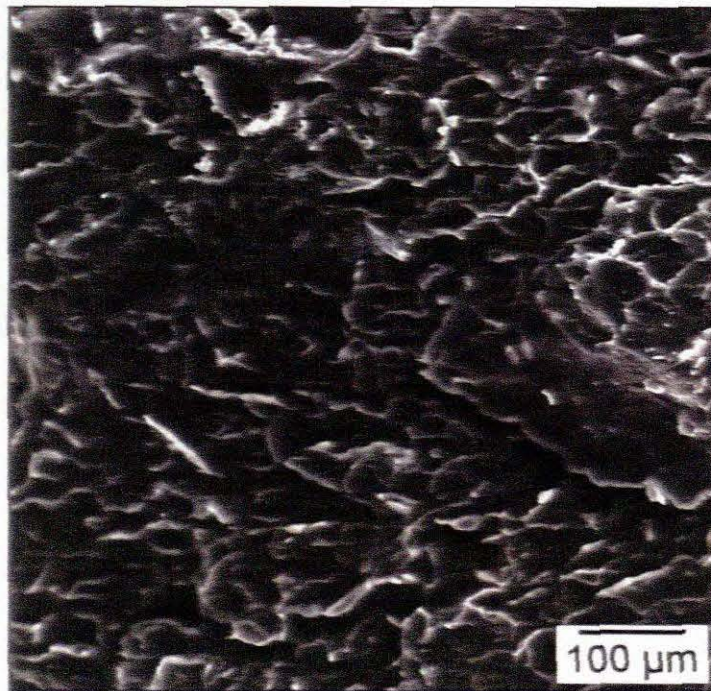


Figure 24: A 1/0.6



### 3.5.2. Fracture surfaces of the fibre reinforced specimens

The fibres used for this study are pre-impregnated with BIS-GMA resin. Figure 25 shows a SEM picture of a fibre bundle that was pre-impregnated and polymerised by light, ready to be placed in a specimen. The image shows the fibres of the bundle joined together and covered by the impregnation material.

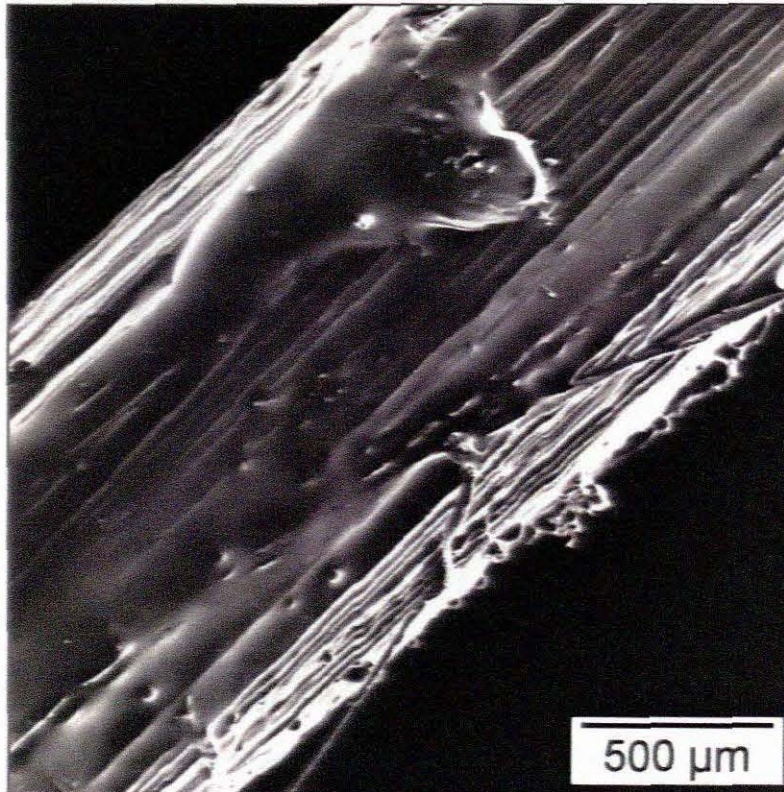
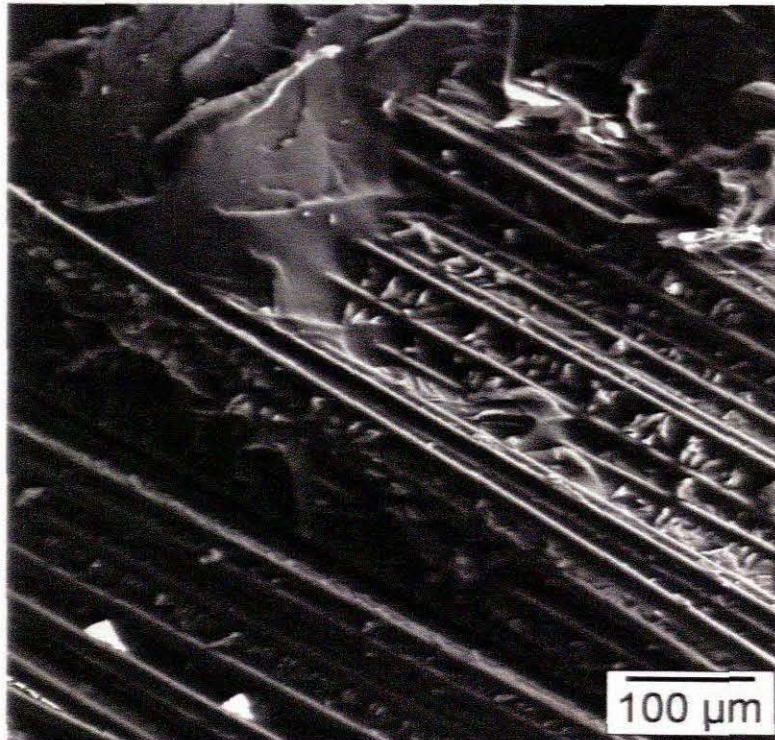


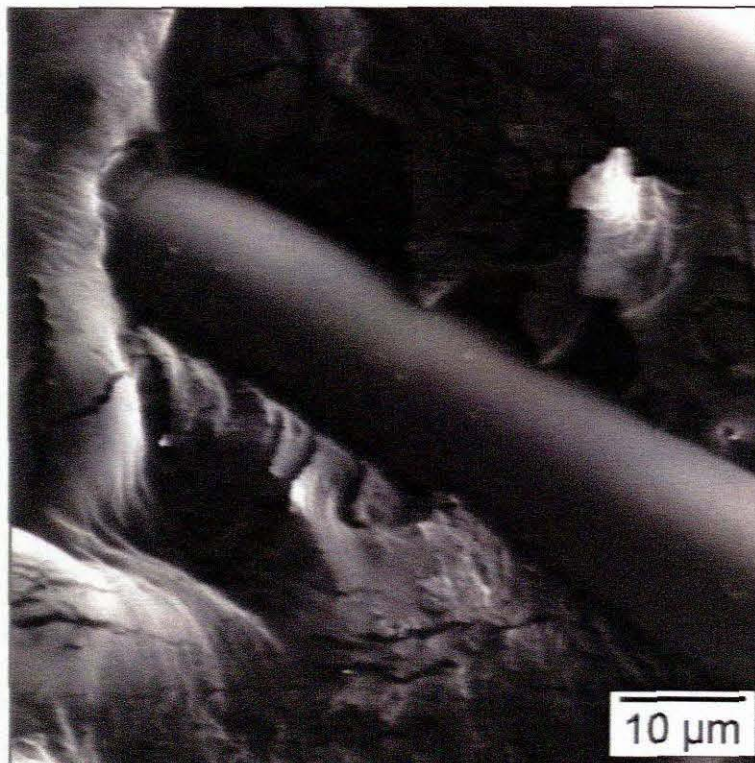
Figure 25: SEM image of the pre- impregnated light-cured fibre bundle.  
(X 50 magnification)

Figure 26 demonstrates what happened to the fibre bundle after it was incorporated in PMMA and subjected to compression using the bending test. The image shows fragments of BIS-GMA resin on the surface of the fibre bundle as well as tags of BIS-GMA resin remaining in between the individual fibres. In between the tags and fibres are voids that indicate the loss of BIS-GMA resin.



**Figure 26: BIS-GMA fractures away from fibres in a specimen of subgroup B 1/1.  
(X 169 magnification)**

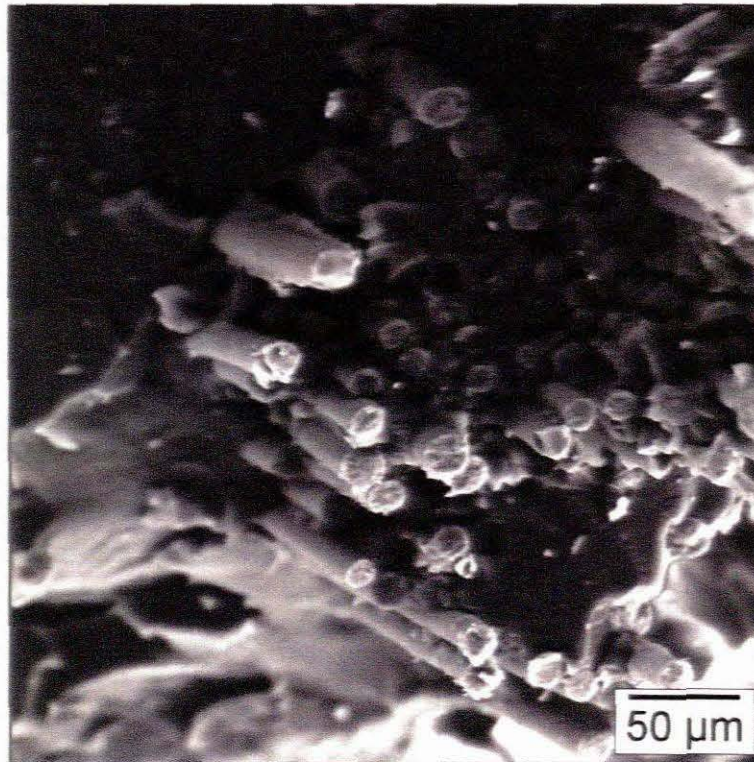
Figure 27 demonstrates the surface of one of the fibres from the previous picture. The surface of the fibre is smooth and shows no sign of damage in the process of the BIS-GMA being torn from the fibres within the bundle.



**Figure 27: SEM image of the surface of a fibre in a specimen of group B.  
(X1700 magnification)**

This type of fracture occurred in the majority of specimens from subgroups B 1/0.6 and B 1/1.

In subgroup B 1/1.5 it was observed that failure of the fibre bundle happened according to fracture type 2, as illustrated in figure 28. In this subgroup the majority of the specimens fractured into two different pieces; figure 13 illustrates one of these pieces.



**Figure 28: SEM image of fractured fibres. (X 300 magnification)**

The fractured fibres are still embedded in the BIS-GMA impregnation material.

The SEM investigation was successful in illustrating the results of the fracture patterns in both groups and in each of the different P/L ratios.

## CHAPTER FOUR

### DISCUSSION

In this study the flexural strength of a PMMA for provisional FPDs was tested in 2 different groups, with 3 different P/L ratios within these 2 groups. One P/L ratio in each group was the manufacturers recommended ratio. One group had no reinforcement and the other group was reinforced with glass fibre.

The null hypotheses tested were that a lower or a higher than the recommended P/L ratio decreases the flexural strength of glass fibre reinforced PMMA provisional FPD material. This hypothesis can be confirmed for both a lower and a higher than the recommended P/L ratio.

The method used to determine the flexural strength was a simple compression test using 3-point bending with the load perpendicular to the long axis of the specimen. The highest stress value before specimen failure was used to calculate the flexural strength. During a compression test, the specimen is subjected to tension, compression and shear stresses. The specimen is weakest in the tensile mode (part of specimen furthest away from the load) and it has been shown that the positioning of the fibre in this part of the specimen or restoration has the highest reinforcement potential (Nohrstrom et al., 2000). For this reason, the fibres were placed in the tensile part of the specimen. To achieve this, the template was provided with two distal stops, 2mm deep, to aid in the positioning of the fibre bundle in the tensile part of the specimen, repeating the same position for each specimen.

For the purpose of this study, the fibre bundle was polymerised before positioning in the specimen. This differs from clinical practice, where the fibre is first adapted to the shape of the restoration, then polymerised. The effect of this modification on the flexural strength is not known, but because it was standard procedure for all the specimens, the study would still allow comparison between the subgroups of group B. It would be interesting to investigate if there is a difference in flexural strength between groups with a wet/wet compared to a wet/dry procedure. There is no known literature available on this aspect.

Within the limits of this experiment, the results indicated that the average flexural strength of all the reinforced subgroups within group B was significantly higher compared to all the unreinforced subgroups of group A. These results mean that the use of fibres is recommended if the strength of PMMA needs to be enhanced.

Although the mean flexural strength values of the three different subgroups within group A did not differ significantly, ratio 1/0.6 had the highest mean value. This means that the stiffer mixture resulted in a slightly, but not significantly, stronger specimen. These results indicate that the P/L ratio does not have a significant effect on the flexural strength of unreinforced autopolymerising PMMA resin materials. The handling property of each of these three ratios differs. Based on these results, it is possible to say that practitioners can be allowed to change the consistency of the mixture to suit the clinical situation without detrimental effect to the flexural strength.

For group B, the scenario is different. The recommended ratio of 1/1 had the highest mean value. There was a significant difference between this subgroup (1/1) and the two other subgroups with ratios 1/1.5 (wetter mix) and 1/0.6 (drier mixture), with lower flexural strength values. There was no significant difference between the ratios of 1/1.5, and 1/0.6. This means that it is important to follow the manufacturer's prescribed ratio if glass fibre is incorporated into the mixture.

Syme et al., (2001), found that while the stiffness of autopolymerising resins was unaffected by variations in P/L mixing ratio, extension to failure was greater with lower P/L ratios. The same results were found in this study. This is easy to see from the graphs in figures 16, 17 and 18.

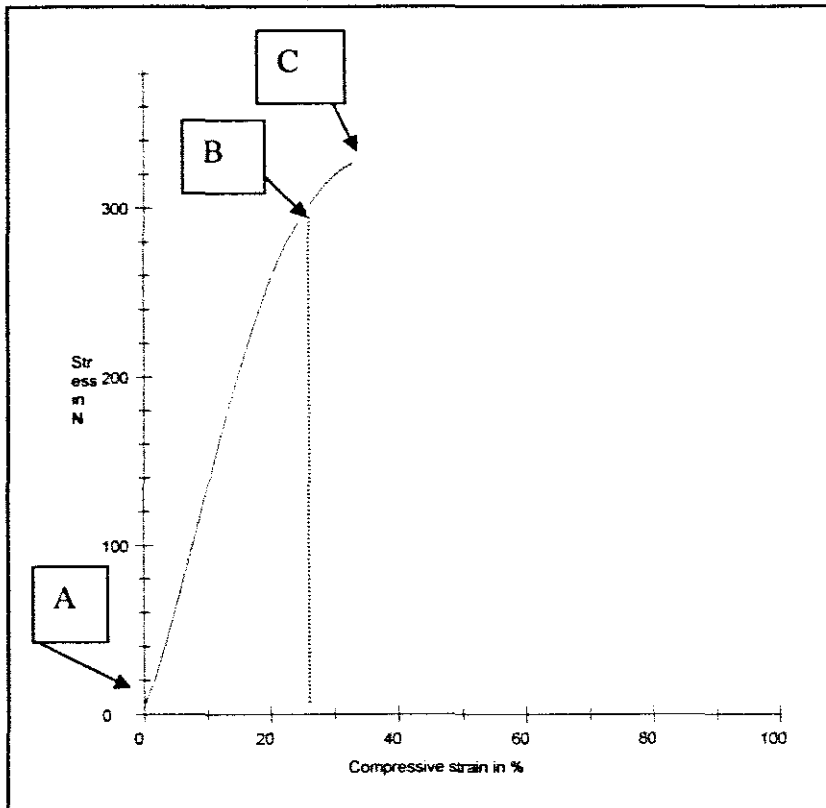
While the literature reports on the effects of a higher liquid content, not much work has been done on a higher powder content. This study can report that although mixtures with higher powder content were slightly stiffer and stronger than the more runny mixtures, this difference was not significant.

Results of a previous study done by Kim and Watts (2004) found no significant decrease in the fracture toughness of their reinforced test groups after 2 months of water storage.

It is interesting to compare the different fracture patterns with the flexural strength values for each subgroup in group B. The recommended ratio 1/1 and the drier mixture of 1/0.6 had the same dominant fracture pattern: the fibre bundle was torn out of the specimen which would suggest that the weakest link in the specimen was between the fibre bundle and the PMMA matrix.

For the wetter mixture of 1/1.5 the fracture pattern was different: the fibres remained inside the PMMA matrix and broke off at the fracture interface, which suggests that the adhesion between the fibre bundle and the wetter PMMA is stronger than the fibre itself. However, the flexural strength of this mixture was lower compared to the other ratios within group B. This difference was significant between ratios B 1/1.5 and B 1/1. This is difficult to explain in terms of the findings of Nohrstom et al., (2000) who said that the transfer of stress takes place from the weaker polymer matrix to the fibre with a higher tensile strength; the better the adhesion between the fibres and the matrix of the resin, the greater the strengthening effect. It is also difficult to explain in terms of Vallittu (1999) who claimed that increased polymerisation shrinkage with wetter mixtures might cause voids along the fibre bundle impacting negatively on the adhesion of the PMMA to the fibre bundle.

Figure 29 is the stress-strain graph of a specimen with a type 1 fracture with the ratio 1/1 within group A. The graph can be explained as follows: Between point A and B the force is going up and elastic deformation occurs, point B is the proportional limit. Between point B and point C plastic deformation occurs. At point C the specimen breaks in two pieces. (type 1 fracture)



**Figure 29: Stress strain graph of a specimen from group A 1/1**

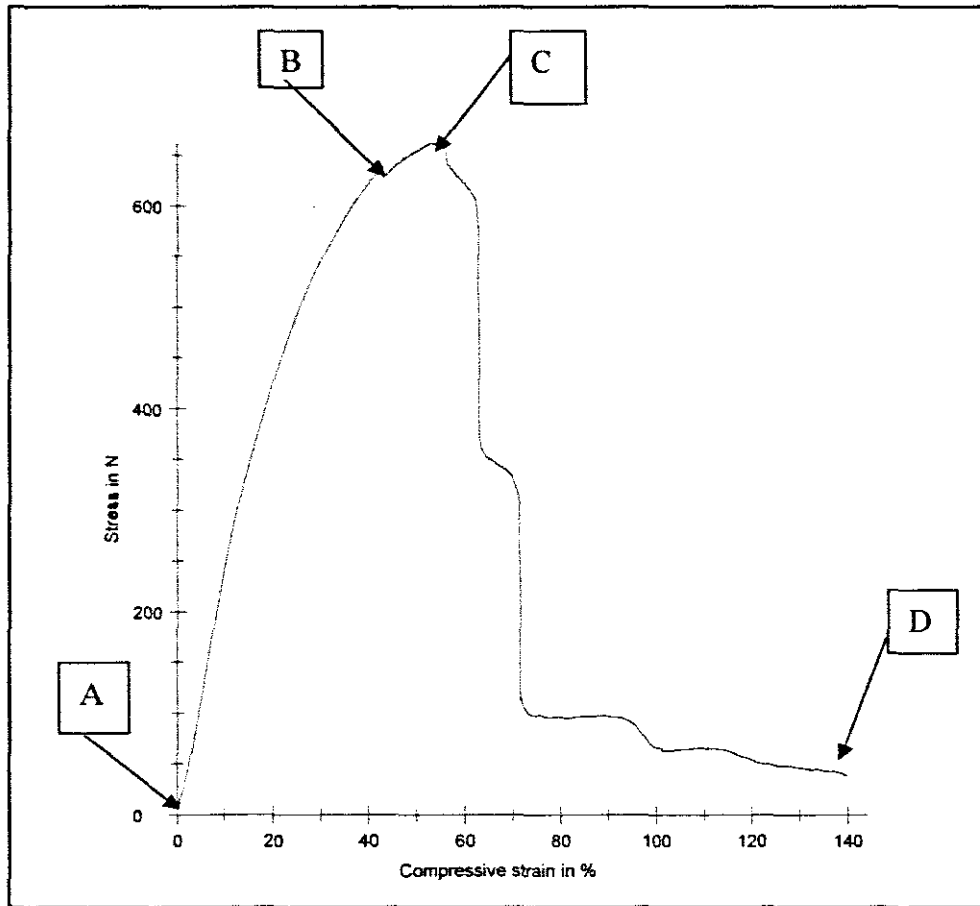
In figure 30 the stress and strain graph of a single specimen with a combination fracture of types 1, 3 and 4 in the ratio 1/0.6 is shown to indicate exactly what happens during the breaking of a specimen when reinforced with a fibre.

Between point A and point B the force on the specimen is going up, at point B the PMMA matrix of the specimens cracks, but the force is still going up after a very small decline. At this point the fibre is still adhered within the PMMA.

At point C the maximum force is reached, and after this point the stress within the specimen starts to decline. This is due to loss of adhesion between the fibre and the PMMA. At point D the specimen is broken, but the fibre is not



broken into two parts, it only pulled out of the specimen. An example of this method of failure is shown in figure 15.



**Figure 30: Stress strain graph of a specimen from group B 1/0.6**

Limited studies have been done on the significance of the variation of the P/L ratios of fibre reinforced PMMA resins. The results of this study show that more needs to be done to fully understand and explain the effect of different P/L ratios on the adhesion of the PMMA mixture to the glass fibre bundle and the resulting flexural strength of the material.

### **Limitations of the study:**

1. **Laboratory study:** This experiment was done in a laboratory using a static load. In the oral cavity, FPDs are subjected to dynamic loads over a period of time. Cyclic loading was not done before the testing of the specimens. Therefore, the results of this study should be considered exploratory and could be the basis of further investigations.
2. **Water storage:** The specimens tested were not stored in water before testing.
3. **SR Ivoron PMMA material:** Only one type of PMMA resin was used in this experiment. It is not advisable to test one commercial product and extrapolate these results to the whole group of materials (PMMA resins).
4. **Direction of fibres:** A possible limitation of this study is the direction of placement of the fibres within the specimens. In this study the fibres were placed unidirectionally and previous studies have shown that multidirectional fibres can further increase the strength of materials. Also, changes in P/L ratios might affect different configurations of fibres differently.
5. **The fibre bundle was light-polymerised before incorporation into the PMMA matrix.** This differs from clinical practice, where the unpolymerised fibre bundle is adapted to the PMMA. This was done to ensure identical position of the fibre bundle in each specimen.

### **Possible further studies:**

1. The bond between the fibres and the impregnation material can be the topic of further investigation, because during the course of this study it has been found that there is a weakness in the bond between the fibres and the BIS-GMA resin it has been impregnated with. In the SEM investigation it can clearly be seen that the fibres came loose or pulled out clean and smooth from the impregnation material.
2. The investigation of the effect of different P/L ratios on different brands within the same group of materials to see if the same tendency exists among different brands.
3. To repeat the study using smaller increments of changes in P/L to see if the effect of changes in P/L ratio on flexural strength is a gradual phenomenon.
4. Since the impregnation of unidirectional and multidirectional fibres may differ, the effect of different P/L ratios on the flexural strength of provisional materials reinforced with multidirectional fibres can be investigated and compared with different P/L ratios of materials reinforced with unidirectional fibres.
5. The project can be repeated using dyed PMMA to analyse the fracture patterns more accurately.
6. The efficacy of impregnation between pre-impregnated and not-pre-impregnated fibres can be compared by means of flexural strength testing and microscopic examination of the fracture patterns.
7. To study the effect of pre- polymerisation of the fibre bundle on the strength of the PMMA compared to unpolymerised fibre bundles.

## CHAPTER FIVE

### CONCLUSION AND RECOMMENDATIONS

#### 5.1 Summary and recommendations

5.1.1 All the subgroups of the glass fibre reinforced group were significantly reinforced compared to their corresponding ratios in the non-reinforced group.

Therefore, it is recommended that glass fibre is used whenever additional strength is required.

5.1.2 Within the non-reinforced group, the dryer mixture gave the highest flexural strength, but the differences between the three subgroups within this group were not significant. Therefore, the practitioner can change the P/L ratio to improve handling properties for certain applications, without detrimental effect.

5.1.3 Within the reinforced group, the P/L ratio as recommended by the manufacturer gave the best reinforcement. The mean flexural strength for this subgroup was significantly higher than that for the drier or wetter mixture. Therefore, when glass fibres are incorporated in the mixture, it is recommended that the prescribed P/L ratio be used.

5.1.4 The successful adhesion between fibre and polymer has been an important contributing factor of increased strength. The present study combined flexural strength testing and SEM analysis of the fractured surfaces of the broken specimen. From the SEM analysis, the group with the lowest mean flexural strength appears to show better-integrated fibres. This contradicts the concept of better adhesion, higher strength. Therefore, the effect of adhesion between fibre bundle and PMMA matrix is not well understood. Even though adhesion between the wetter mixture PMMA and the fibre bundle appears to be better judged according to the fracture pattern, this did not reflect in higher flexural strength values.

## 5.2 Conclusion

Little literature could be found on the influence of changing P/L ratios on the strength of PMMA material. These studies show that the different P/L ratios have no significant effect on the mechanical properties of unreinforced polymers.

To date, no literature could be found on the influence of changing the P/L ratios on the mechanical properties of reinforced polymers.

Within the limitations of this study the results demonstrate that for reinforced polymers, the P/L ratio should not be changed. For glass-fibre reinforced PMMA, using a different than the recommended P/L ratio has a detrimental effect on the flexural strength of the polymer compared to the manufacturers recommended P/L ratio. Therefore, it is important that the manufacturers recommended ratio be used with glass-fibre reinforcement.

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[Accessed-29 September 2007]



## **Appendix A: Product specifications of the SR Ivocron®**

### **Description**

SR Ivocron is a PMMA veneering material. Depending on the indication and the monomer used, SR Ivocron can be used in conjunction with the cold, hot, or pressing technique.

### **Indication**

#### **Cold technique (pouring technique)**

- For short- or medium-term temporaries
- Securing of ground denture teeth on the cast framework
- Repairs

#### **Hot technique (layering technique)**

- Crown and bridge veneering technique

#### **Pressing technique (flasking technique)**

- Crown and bridge veneering technique

### **Contraindication**

Direct use in the oral cavity

### **Composition**

#### **SR Ivocron Dentin, Incisal, Cervical, and Intensive Powders**

consist of polymethyl methacrylate (> 98 % wt.), catalysts, and pigments (< 2 % wt.).

#### **SR Ivocron Opaquer Powder**

consists of copolymer, aluminium oxide, barium sulphate, and titanium dioxide (> 98 % wt.), as well as catalysts and pigments (< 2 % wt.).

#### **SR Ivocron Opaquer Liquid**

Methyl methacrylate □99 % wt., catalysts □1 % wt.

### **Side effects**

Systemic side effects are not known to date. In individual cases, allergic reactions to PMMA materials have been reported.

### **Warning**

SR Ivocron Opaquer Liquid, as well as the Cold, Hot, and Press Liquids contain methyl methacrylate. MMA is irritant and highly flammable (flash point: 10 °C/50 °F). Do not inhale vapours. The material irritates eyes, respiratory organs, and skin. Skin contact may lead to sensitization. For further information, please refer to the EEC safety data sheet (or MSDS).

**Summary of the most  
important data**

**Cold Technique**

**Mixing ratio by volume**

1 part polymer : 1 part monomer

**Mixing ratio in g**

1 g polymer : 0.83 g monomer

**Dough time**

3-4 minutes

**Working time at 23 °C (73 °F)**

Approx. 8 minutes

**Polymerization**

In the pressure apparatus at 2–6 bar pressure and  
40–50 °C (104–122 °F) for 15 minutes

## Appendix B: Raw data of the different groups

### Group A (no fibre)

#### subgroup P/L 1/1

Nr	a0 mm	b0 mm	Fmax N	F{lo Break} {epsilon}Break{epsilon}-F max N	mm	mm
1	6.166	3.016	415.54	415.54	1.46	1.46
2	6.084	3.027	287.29	287.29	0.85	0.85
3	5.98	2.95	272.15	272.15	0.72	0.72
4	6.12	3.093	305.33	305.33	0.95	0.95
5	6.18	3.008	368.5	350.31	1.19	1.19
6	6.1	2.98	313.22	313.22	1.07	1.07
7	6.2	3.006	406.64	406.32	1.59	1.59
8	6.19	3.026	363.95	363.95	1.09	1.09
9	5.95	2.96	413.99	413.88	1.35	1.35
10	6.1	2.99	358.4	345.01	1.45	1.45
11	5.9	2.91	363.73	355.76	1.36	1.36
12	6.15	3.06	421.83	420.96	1.46	1.46
13	6.06	2.97	370.19	369.44	1.22	1.22
14	5.98	2.92	371.31	371.31	1.2	1.2
15	5.98	2.94	316.47	302.26	0.86	0.85
16	6.04	2.99	412.01	412.01	1.36	1.36
17	5.98	2.98	340.38	329.45	1.06	1.06
18	6.03	2.93	393.29	375	1.52	1.52
19	5.9	2.95	334.53	320.83	1.02	1.02
20	6.005	3.01	361.1	359.96	1.23	1.22
	<b>6.05</b>	<b>2.99</b>	<b>359.49</b>			

**Group A (no fibre)**  
**subgroup P/L 1/1.5**

Nr	a0 mm	b0 mm	Fmax N	F{lo Break} {epsilon}Break {epsilon}-F max N	mm	mm
1	5.83	2.8	308.03	302.87	1.49	1.48
2	5.9	2.89	308.34	308.34	1.23	1.23
3	5.79	2.9	311.3	311.3	1.82	1.82
4	5.91	3.09	323.73	321.8	1.19	1.19
5	6.06	2.98	303.42	299.04	1.06	1.06
6	6.16	2.9	377.46	377.46	1.38	1.38
7	5.8	3.1	213.23	213.23	0.73	0.73
8	6.2	3.06	432.13	431.55	2.04	2.03
9	5.9	2.7	284.49	271.42	1.17	1.17
10	6	2.81	401.76	390.75	1.85	1.83
11	5.95	2.72	348.94	344.11	1.12	1.12
12	6.04	2.69	380.07	371.26	1.42	1.42
13	6.1	2.8	355.23	355.23	1.43	1.43
14	5.9	2.85	261.93	261.93	0.78	0.78
15	5.99	2.83	416.06	413.38	2.15	2.02
16	6.2	2.79	309.81	309.81	1	1
17	6.12	2.73	326.95	326.95	1.57	1.57
18	6.21	2.91	355.16	352.55	1.57	1.57
19	6.02	2.84	301.23	287.43	1.34	1.34
20	6.17	2.78	351.68	351.55	1.48	1.48
21	6.09	2.89	356.26	338.27	1.61	1.6
	<b>6.02</b>	<b>2.86</b>	<b>334.63</b>			

**Group A (no fibre)**  
**subgroup P/L 1/0.6**

Nr	a0 mm	b0 mm	Fmax N	F{lo Break} {epsilon}Break {epsilon}-F max N	mm	mm
1	6.02	2.83	376.12	364.62	1.41	1.41
2	6.003	2.71	296.67	296.67	0.96	0.96
3	5.9	2.87	350.37	350.37	1.29	1.29
4	5.91	2.77	331.07	331.07	1.07	1.07
5	5.98	2.82	367.46	350.86	1.4	1.4
6	6.03	2.73	355.2	355.2	1.13	1.13
7	6.1	2.8	368.07	368.07	1.75	1.75
8	5.91	2.79	338.03	338.03	1.36	1.36
9	5.97	2.68	354.74	353.34	1.32	1.32
10	6.03	2.67	311.59	311.59	0.99	0.99
11	5.99	2.82	354.18	354.18	1.26	1.26
12	5.87	2.74	341.87	341.87	1.27	1.27
13	6.01	2.81	342.59	342.59	1.49	1.49
14	5.93	2.69	290.08	290.08	1.17	1.17
15	6.005	2.89	357.13	349.95	1.22	1.22
16	6.004	2.79	284.83	284.83	0.87	0.87
17	6.01	2.81	324.82	317.92	1.15	1.14
18	5.91	2.79	307.41	299.18	1.18	1.18
19	5.97	2.82	326.67	319.91	1.29	1.29
20	6.07	2.73	314.62	314.5	1.02	1.02
21	5.92	2.83	307.67	307.67	0.88	0.88
	<b>5.98</b>	<b>2.78</b>	<b>333.39</b>			

## Group B (with fibre)

subgroup P/L 1/1

Nr	a0 mm	b0 mm	Fmax N	F{lo Break} N	{epsilon}Break{epsilon}-F max mm	F max mm
1	6.2	3.09	721.48	503.17	3.27	2.88
2	6.1	3.1	572.54	141.35	2.19	1.44
3	5.91	2.89	579.29	28.94	4.47	2.52
4	5.97	2.81	661.73	41.92	4.46	2.5
5	5.9	2.91	693.9	492.04	3.72	2.81
6	5.84	2.7	514.65	15.43	3.63	1.58
7	5.79	2.83	590.37	376.82	4.06	3.01
8	5.85	2.85	709.49	705.04	2.46	2.44
9	5.92	2.74	589.77	461.51	3.45	2.48
10	6.2	2.9	723.14	704.78	3.05	2.92
11	6.05	2.75	653.22	302.6	4.54	3.29
12	5.99	2.82	564.81	477	3.4	2.16
13	6.12	2.93	654.71	7.47	6.96	2.89
14	6.15	2.77	603.98	372.22	4.37	3.06
15	6.2	2.83	567.59	10.31	9.65	2.7
16	6.19	2.89	603.29	543.13	3.45	2.59
17	6	2.7	616.87	14.46	9.74	3.04
18	6.02	2.82	613.07	317.31	3.31	2.54
19	6.06	2.91	416.36	259.91	2.07	1.71
20	6.1	2.81	488.71	20.9	5.05	2.31
21	6.09	2.78	486.08	348.61	2.44	1.98
	<b>6.02</b>	<b>2.85</b>	<b>601.19</b>			

**Group B (with fibre)**  
**subgroup P/L 1/1.5**

Nr	a0 mm	b0 mm	Fmax N	F{lo Break} N	{epsilon}Break mm	{epsilon}-F max mm
1	6.17	2.8	602.05	408.51	4.17	3.07
2	6.2	2.92	570.72	329.88	3.73	2.55
3	6.05	2.83	566.16	359.01	4.21	2.7
4	6.19	2.81	563.27	459.83	3.7	2.74
5	6.17	2.88	593.14	390.81	3.64	2.23
6	6.07	2.79	570.63	394.24	4.77	2.7
7	6.05	2.91	492.45	298.64	2.58	2.22
8	6.12	2.95	531.34	323.05	3.46	2.65
9	6.09	2.88	595.27	494.9	3.53	2.48
10	6.2	2.85	537.1	280.48	4.25	2.45
11	6.13	2.79	570.98	407.07	4.1	2.82
12	6.03	2.88	554.89	554.89	2.21	2.21
13	6.13	2.99	593.76	97.05	4.03	2.42
14	6.06	2.89	587.98	-	-	3.1
15	6.07	2.82	549.31	409.82	4.1	3.02
16	6.2	2.79	390.14	276.18	2.88	1.98
17	6.19	2.83	466.56	299.29	3.03	1.89
18	6.2	2.71	431.9	322.91	2.8	1.68
19	6.11	2.85	423.04	318.68	2.08	1.81
20	6.21	2.94	557.58	304.49	3.83	2.34
21	6.2	2.79	454.28	349.17	2.14	2.11
	<b>6.13</b>	<b>2.85</b>	<b>533.45</b>			

**Group B (with fibre)**  
**subgroup P/L 1/0.6**

Nr	a0 mm	b0 mm	Fmax N	F{lo Break} N	{epsilon}Break mm	{epsilon}-F max mm
1	6.1	2.79	652.53	563.31	3.67	2.81
2	6.19	2.88	622.04	316.19	4.15	2.88
3	6.02	2.75	662.26	38.43	8.14	3.1
4	6.009	2.93	562.13	445.51	3.35	2.53
5	6.1	2.89	635.27	30.07	5.29	2.76
6	6.21	2.91	757.52	491.3	4.08	3.37
7	6.17	2.9	545.28	5.44	8.95	2.63
8	6.08	2.87	602.18	461.79	3.56	2.53
9	6.15	2.86	591.46	361.22	4.62	3.25
10	6.22	2.93	659.5	643.55	2.38	2.37
11	6.12	2.81	603.63	451.77	2.76	2.06
12	6.18	2.78	583.08	583.08	2.87	2.87
13	6.07	2.83	636.7	313.53	4.58	3.22
14	6.19	2.89	411.43	-	-	1.72
15	6.17	2.77	597.81	352.94	4.39	2.65
16	6.2	2.91	344.11	12.63	4.45	1.69
17	6.2	2.71	489.16	477.58	2	1.83
18	6.1	2.83	471.23	70.94	4.24	1.96
19	6.19	2.85	397.48	397.31	1.33	1.33
20	6.13	2.91	348.14	70.2	5.51	1.3
	<b>6.13</b>	<b>2.85</b>	<b>558.647</b>			