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# DEVELOPMENT OF LONG FIBRE HEAT CURE PHENOLIC DOUGH MOULDING COMPOUNDS

by

## **KRISTOF DEBRABANDERE**

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of the Loughborough University of Technology

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### **SYNOPSIS**

Traditionally, dough moulding compounds (DMCs) have been based on unsaturated polyester resins (UPR), fillers and glass fibre reinforcements. Such systems however are inflammable and will emit dense, toxic smoke on combustion.

Phenolic resins, on the other hand, have excellent flame retardant properties, but slightly inferior mechanical properties. Phenolic DMCs are based on mineral fillers and glass fibre reinforcements, compounded into a phenolic resol (heat cure) resin. Compounding these systems using a co-rotating twin screw extruder, instead of the traditional method using a Z-blade mixer, results in long fibre DMCs which have better mechanical properties than short fibre DMCs.

In this study, a wide range of inorganic materials, their pH being one of the selection factors, have been investigated as potential phenolic DMC fillers. Viscosity measurements were carried out on resin/filler mixtures, while on the cured samples flexural and impact properties were investigated. Producing DMCs using a twin screw compounder, the effects of filler loading, types of glass fibre, glass fibre loading and machine output on flexural and impact properties were investigated.

Phenolic dough moulding compounds containing 20 wt % high integrity glass fibres and small amounts of aminosilane treated china clays (40 phr filler) had superior mechanical properties. These systems have a flexural strength of more than 120 MPa, which would allow them to compete with traditional UPR-based DMCs.

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## CHAPTER 1 INTRODUCTION

#### 1.1 GENERAL BACKGROUND

Moulding compounds are mixtures of a thermosetting resin such as polyester or phenolic resin, filler(s) such as clay, calcium carbonate, etc and reinforcing fillers such as glass fibre or woodflour.

Moulding compounds were first developed in the early fifties. However, commercial products were not available for another decade. Originally, moulding compounds were based on unsaturated polyester resins, filler and cellulosic reinforcements. Subsequently with the introduction of glass fibre as a reinforcement, rapid growth occured in the usage of polyester moulding compounds.

In the early eighties, phenolic resins for fibre reinforced plastics (FRP) were commercially introduced. The excellent fire performance of phenolic resin, combined with low smoke and toxic fume emission (Figure 1.1) and good high temperature stability (Figure 1.2) at a competitive cost compared to polyester and epoxy resins, has ensured it an ever increasing market share [Knop and Pilato]. This new generation of reinforced phenolic resins is being used in automotive, mining, mass transit, construction and leisure applications, i.e. fire critical and high temperature applications [Forsdyke, Hunter and Forsdyke]. The fire disaster in King's Cross underground station in London in 1987 emphasised the need for materials with superior fire and smoke performance. More recently, phenolic resins have been combined with glass fibre and fillers to constitute moulding compounds. However, in traditional moulding compounds, superior mechanical properties are obtained using unsaturated polyester resin (UPR)-based systems. Dough moulding compounds (DMC), i.e. moulding compounds with a certain composition (see Section 1.2) and the consistency

of a dough are produced using a Z-blade mixer. This compounding method inherently involves fibre breakdown and produces short fibre DMC. Such a compound has relatively poor mechanical properties.

A method by which long fibres may be incorporated into phenolic resins involves the use of a twin screw compounding extruder. This process can result in less fibre damage and can therefore be used to prepare long fibre DMCs which have better mechanical properties than short fibre DMCs. This could lead to a group of phenolic moulding compounds having mechanical properties comparable to standard polyester resin systems, but with the advantage of superior fire performance.



Figure 1.1: Smoke density of thermoset resins (NBS Smoke Chamber - smouldering) [Forsdyke]



Figure 1.2: Flexural strength of fibre reinforced thermoset resins in relation to temperature [Knop and Pilato]

#### 1.2 GENERAL COMPOSITION OF MOULDING COMPOUNDS

Phenol-formaldehyde (PF) moulding compounds consist essentially of phenolic resin, filler(s) and glass fibre. The glass fibre confers most of the mechanical strength to the material, the effect of filler being secondary in this respect, contributing only slightly to strength. In addition to acting as an extender to lower the cost, the filler does have a very important role in the formulation of these materials. The filler modifies the oligomer matrix (resin/filler) viscosity so that fibre separation or filtration does not occur during normal moulding conditions [Burns].

Two types of moulding compound have been developed: sheet moulding compound (SMC) and dough moulding compound (DMC). A basic difference between SMC and DMC is that the latter is a fairly simple mixture of the ingredients whereas the former is made by laying a paste mixture of resin and filler,

on to a carrier film of polyethylene or polyamide, subsequently covering this with chopped glass fibre and then laying another layer of the resin/filler paste on top of this followed by another carrier film of polyethylene. The manufacturing process is continuous with the formed "sandwich" being taken up on a roller which compacts it. Normally, polyester SMC undergoes a maturation period in which time its viscosity increases by several decades. In use, DMC is a dough-like material while SMC is a sheet material. For this reason, SMC is easier to handle and ideal for two-dimensional mouldings with large surface areas. SMC is chemically thickened, allowing higher glass fibre contents which gives the compound a higher strength. Glass fibre length with SMC is typically 25 mm, up to a maximum of 50 mm.

DMC, or BMC (bulk moulding compound) as it is known in the USA, has higher filler levels and lower fibre and resin levels than SMC. The length of fibres is typically 6 mm with a maximum of 12 mm [McDonald]. Therefore, although properties of DMC are relatively uniform in all directions, i.e. isotropic, it tends to be weaker than SMC.

Sheet moulding compounds are generally available with glass contents in the range of 20 - 40 %. Below 20 %, control of glass fibres becomes difficult during moulding, and unconsistency is a problem. At about 40 % glass content, wetting out of fibres becomes difficult and it is found that very low resin/filler (slurry) viscosities are necessary which in turn give problems during storage and manufacture.

Dough moulding compounds are not normally formulated to contain over 25% glass fibre because, above this level, fibre attrition during mixing becomes so great that very little advantage in strength properties is achieved. Typical commercial formulations for PF and UPR SMC and DMC are given in Table 1.1. Table 1.2 illustrates the effect of fibre content on the mechanical properties of polyester moulding compounds.

TABLE 1.1: Typical composition of basic moulding compounds

Ingredient	Conten	t (wt %)
	DMC	SMC
Thermosetting resin Filler Glass fibre Thickening agent	25 55 20 -	31 30 37 2

TABLE 1.2:	The effect	of glass	fibre	content	on	mechanical	properties	of
	polyester d	lough moi	ulding	compou	nds	. [Burns]		

Property	Glass/Fibre Content (wt %)		
	15	22	30
Tensile strength (MPa) Flexural strength (MPa) Flexural Modulus (GPa) Izod impact (kJ/mm <sup>2</sup> ) Compressive strength (MPa)	31 97 8.3 4 117	38 103 10.3 5 135	45 114 12.4 6.5 148

TABLE 1.3: Comparison between polyester and phenolic resin moulding compounds. [Burns, Composites]

Type of	Flexural	Tensile	Compressive	Izod impact
moulding	Strength	strength	strength	strength
compound	(MPa)	(MPa)	(MPa)	(see below)
UPR DMC	88	32	127	4.5 (ftlb/in)
UPR SMC	193	101	166	13.4 (ftlb/in)
PF DMC	100	30	300	250 (J/m)
PF SMC	150	60	-	300 (J/m)

The rapid growth in use of both SMC and DMC since the mid-sixties has been largely due to the flexibility in formulation and their all-round combination of properties.

#### 1.3 OBJECTIVE

The main objective of this work was to develop simple, long fibre moulding compound formulations, based on heat curable phenol-formaldehyde resol resin, mixed with mineral filler and glass fibre currently available at competitive prices.

These compounds must have mechanical properties comparable to unsaturated polyester resin dough moulding compounds.

# CHAPTER 2 LITERATURE SURVEY

#### 2.1 MATERIALS

#### 2.1.1 Resin

#### 2.1.1.1 Brief history

The fact that phenol and formaldehyde, when mixed together, undergo a reaction that results in a hard, infusible and insoluble polymer, has been known for a considerable time [Lubin].

However, it was not until L. Baekeland introduced his "heat and pressure" patent in 1907 that the production of phenol-formaldehyde (PF) moulded parts became economically viable [Baekeland]. This makes phenol-formaldehyde the oldest man-made polymer. When originally marketed, this material was called "Bakelite", a tradename given in honour to the inventor and this name persists in the minds of the public as a common term for all plastics.

#### 2.1.1.2 Chemistry of phenolic resins

The term phenolic resin is used to classify a range of resins that can be synthesised from different phenols, e.g. phenol, cresol, xylenol, resorcinol and aldehydes, e.g. formaldehyde, acetaldehyde and propionaldehyde. However, phenol and formaldehyde are the most widely used ingredients for a reasonable wide range of phenolic resin materials [Knop and Pilato].

Phenolic resins are obtained by step-growth polymerisation of difunctional monomers (aldehydes) with monomers which potentially have functionality greater than two (phenols).

Three reaction sequences must be considered:

- formaldehyde addition to phenol,

- chain growth or prepolymer formation and
- the crosslinking or curing reaction [Sebenik et al, 1974].

Depending on the reaction conditions, two distinct types of phenolic resin oligomers or pre-polymers may be produced, i.e. novolaks and resols.

#### Novolaks

Novolaks are prepared by reacting phenol and formaldehyde together under acidic conditions using a molar ratio of phenol to formaldehyde greater than one (1.15 to 1.3). Novolaks are linear or slightly branched condensation products, linked with methylene bridges and of a relatively low molecular weight (up to 2000). These resins are soluble and permanently fusible, i.e. thermoplastic, and are cured only by addition of 8-15% of the crosslinking of curing agent or hardener hexamethylenetetramine (HMTA) to insoluble and infusible products. HMTA is a thermally labile adduct of formaldehyde and ammonia. The former is used as crosslinker while the latter is used as catalyst. The crosslinking reaction is accompanied by the liberation of a considerable amount of gas, which consists of at least 95% of ammonia. The HMTA/novolak reaction results in a crosslinked resin, containing up to 6% chemically bound nitrogen. The level of HMTA affects the degree and rate of curing, mechanical and electrical properties, hardness and shrinkage [Chiang and Yang].

#### Resols

Resols are prepared by reacting phenol and formaldehyde together under alkaline conditions using a molar ratio of phenol to formaldehyde of less than one (0.6 to 0.9). Mixtures of mono-, di- and tri- methylphenols can be formed, the degree of substitution being influenced by the molar ratio of phenol to formaldehyde. During the reaction stage, the methylol phenols condense both with themselves and with phenol, eliminating water, to form two, three or more ringed systems, linked by methylene bridges. The formation of dihydroxydibenzyl ether links is not considered likely under alkaline conditions. At the end

#### Chapter 2: Literature Survey

of the reaction stage, liquid resols are generally neutralised and concentrated by vacuum distillation to meet the required viscosity specification. The finished product is a resol with a controlled molecular weight distribution of species, consisting of phenol, methylol phenols and methylene bridged multi-ring methylolated compounds, containing up to ten units. The average molecular weight of a resol is in the 250-1000 range. Water remaining in the resin (approximately 5-13%) acts as a diluent, controlling viscosity in combination with the molecular weight distribution. Resols are transformed into three-dimensional, crosslinked, insoluble and infusible polymers by the application of heat or by the use of acids as catalyst.

In the case of novolaks, polynuclear phenols are linked by methylene groups. Resols contain mainly methylene links and, depending on temperature and pH, a number of dimethyl ether links can be formed [Blinkhorn]. Whilst novolaks tend to be solid, water insoluble materials, resols tend to be viscous liquids which will, to a certain extent, dissolve in water or aqueous alcoholic solutions. Generally, industry considers the oligomerisation of phenol and formaldehyde and subsequent cure to be a two stage process. As such is the secret to successful controlled conversion of monomer to useable polymer.

The resins used in this work were of the resol type. Resol resin formation, i.e. addition of formaldehyde to phenol followed by chain growth, is illustrated in Figure 2.1. Curing, with a relatively strong exotherm, is completed by either the application of heat, i.e. heat cure or the addition of an acid, i.e. acid catalysed cure [Christiansen, King *et al*].



Figure 2.1: Resol resin formation.

#### 2.1.1.3 Manufacture of phenolic resin

Liquid, solid and solvent based resins can be produced from the basic ingredients of phenol and formaldehyde by varying the reaction conditions. Such reaction parameters include:

- molar ratio of phenol to formaldehyde,
- reaction time and temperature,
- type and amount of catalyst,
- water content and residual phenol,
- modification with other aldehydes and/or substituted phenols,
- etherification and/or dissolution in organic solvents,
- modification with other compounds (in order to enhance thermal stability) [Knop and Pilato].

A phenolic resin is produced in a batch process. The multitude of resin specifications required by the market would render any continuous process uneconomical. The batch volume in the production of phenolic resins is limited by the exothermic reaction between phenol and formaldehyde and hence temperature build up. Nowadays, reactors with a capacity of up to 60 cubic metres are used.

The following procedure is an example of the production of a resol on a laboratory scale [Sorenson and Campbell]: a 500 ml resin kettle is equipped with a reflux condenser, stirrer and thermometer. 94g (1 mol) of distilled phenol, 123g (1.5 mol) aqueous formaldehyde 37% by weight and 4.7g barium hydroxide octahydrate are added to the reaction vessel. The reaction mixture is stirred and heated in an oil bath at 70°C for 2 hrs. Sufficient dilute (10%) sulphuric acid is added to reduce the pH to 6-7. Vacuum is then applied and water is removed through a condenser to meet the required viscosity specification. Water remaining in the resin acts as a diluent, controlling viscosity in combination with the molecular weight distribution. Typically, the water content of a resol is in the range of 10-13 %. Further water (2-4%) is introduced with the catalyst (if acid cure) and is also produced during the curing reaction.

#### 2.1.1.4 Physical effects of cure chemistry

During cure, as the molecular weight of the resin increases its water tolerance decreases. The water, dissolved in the resin or produced as condensation product, separates rapidly as discrete droplets and the matrix becomes opaque. These droplets vary in size depending on rate of cure but normally have diameters between 2 and 6  $\mu$ m. A second distribution of smaller holes of circa 1  $\mu$ m diameter are also present. These may be attributed to formaldehyde vapour evolved during cure. At the release stage, the resin matrix is a honeycomb structure of discrete vapour filled voids in the 1-6  $\mu$ m diameter range. Postcuring can be used to remove the majority of the volatiles, resulting

in a micro-porous structure. The small voids in the resin matrix, left by volatiles present during cure, have proven to be beneficial rather than detrimental to the physical properties of the matrix. The small voids are thought to act as areas of energy dissipation [BP Chemicals].

Curing characteristics have been studied by evaluating the hardness of moulded compounds [Tonogai *et al*, 1]. Using the same technique, a curing process based on two types of curing reactions, i.e. propagation and crosslinking, has been proposed [Tonogai *et al*, 2]. Others have proposed a different model for the post bake behaviour of phenolic resins which involves rearrangements of the crosslinked structure [Morrison and Waitkus].

Highly crosslinked resol type resins were found to have three secondary transitions over the temperature range of -250 to +250°C, related to small segment motions [Warfield and Lee].

#### 2.1.1.5 Properties of unfilled phenolic resin

The pH of the phenolic oligomer system not only affects its shelf life but also determines the heat of reaction and exotherm peak temperature [Gupta et al]. Resols are most stable, i.e. have the longest shelf life, when the pH is around 5 [Gupta and Hindersinn]. A higher or lower pH will reduce the resin shelf life. The curing temperature and heating rate affect both the reaction kinetics and the final structure of the crosslinked network [Siegmann and Narkis]. Ageing and humidity are also known to affect the flow and curing characteristics of phenolics [Tonogai and Seto, Tonogai *et al*, 3]. Table 2.1 gives some properties of cured unfilled phenolic resin.

#### TABLE 2.1: Properties of Unfilled Phenolic Resin

Littimete tensile strength (MPa)	62
Olumate tensile strength (wir a)	02
Elastic tensile modulus (GPa)	4
Tensile elongation (%)	1.7
Coefficient of thermal expansion (x 10 <sup>-6</sup> K)	68
Service temperature (°C)	150-230
Density (g/cm <sup>3</sup> )	1.28

#### 2.1.2 FILLERS

#### 2.1.2.1 Introduction

Fillers have been used in plastics for many years. They are added in order to reduce costs and/or, to improve processing and/or, to modify the end-use properties. In moulding compounds, fillers also modify the rheological behaviour of the compound such that uniform flow occurs without resin segregation. This is critical since viscosity of a compound is normally greatly reduced at the moulding temperature. Such a viscosity decrease may cause the glass strands to agglomerate, creating heavily rippled surfaces, flow lines and variable strength properties.

#### 2.1.2.2 Selection and characterisation of fillers

Before selecting a particular filler or filler system, several aspects have to be considered:

- a) How is the filler contributing to the properties of the compound?
   Generally, the effects of filler can be summarised as follows:
  - a reduction in shrinkage,
  - an increase in flexural and tensile moduli,
  - a decrease in flexural and tensile strength at higher filler loadings,
  - a decrease in impact strength and
  - an increase in hardness.

The surface appearance of mouldings can be significantly affected by the choice of filler and particle size distribution.

- b) How is the shelf life of the resin affected?
   Ideally, a neutral or slightly acidic filler would be preferred as some resol resins are most stable at a pH of about 5. Unfortunately, most mineral fillers are alkaline with a pH of up to 9-10, reducing the resin's shelf life.
   The presence of small quantities of metal impurities in a filler will also reduce the shelf life.
- c) To what extent is the curing reaction affected by the filler? Fillers modify the temperature profile by decreasing the amount of heat liberated during the reaction and acting as a heat sink, i.e. volume dilution effects [McGee]. Thus, increasing filler content will slow down the reaction rate, increase the gel time, decrease the maximum centreline temperature in a moulding and therefore increase the maximum allowable mould temperature. Varying the filler content also affects the way a part cures: the cure front can progress towards either the centreline of the moulding, or towards the mould wall or towards both. Mizumachi and Morita discovered that the curing reaction of phenolic resin is retarded by certain types of woodflour filler but not by others [Mizumachi and Morita].

The effects of silane coupling agents on the curing behaviour of phenolic resins have been investigated by [Price and Ku]. Their work showed that the heat of reaction could differ by as much as 50% by changing the type of coupling agent. Obviously, these changes have a significant effect on the internal temperature-time profile and processing time of the composite.

- d) How does the filler affect the fire performance of a compound? Aliphatic-based thermoplastic additives and organic fillers - such as the general purpose PF filler, woodflour - can not be incorporated into fire retardant phenolic moulding compounds as these fillers would jeopardise the overall fire performance of the compound.
- e) When mixtures of fillers are used, is there any interaction between the fillers?

Physical interaction between fillers can be manifested in packing efficiency. Blends of particulate, flaky, spherical, rod-shaped and acicular fillers will result in different packing ratios depending on their relative proportions. It has been shown that particle size distribution (polydispersity) determines packing efficiency [Greenzweig and Pickering]. There is a direct inverse relationship between packing ratio and slurry viscosity [Burns]. The ratio of fractional filler volume to filler packing fraction has an effect on several parameters [Ferrigno]:

- viscosity,
- modulus,
- tensile strength,
- flexural strength,
- compressive strength,
- electrical and thermal conductivity,
- volume cost.

Filler shape can have an effect on the average (glass) fibre length. During compounding, acicular fillers may, as a result of high shear forces, break down fibres.

 f) In the case of mineral fillers: are they abrasive?
 If they are, special precautions may have to be taken in order to prevent excessive wear on the compounding equipment. g) To what extent does filler affect the overall compound cost? Filler is by far the cheapest component in a moulding compound. Filler type, particle size distribution and surface coating all affect slurry viscosity. Therefore, it is sometimes cheaper to incorporate a high-cost-low-absorption filler instead of a low-cost-high-absorption filler so that larger amounts of filler can be used.

Specific gravity can be important when the final product is to be sold by weight or volume. Furthermore, the specific strength of a product is important when fuel efficiency for automotive applications is considered.

h) In the case of very fine powders: is there any danger of dust explosions?
 Extraction units may be required from a health and safety viewpoint.

Once a filler or filler system has been selected it is imperative to characterise the filler(s) so that a compound with reproducible properties can be manufactured. Some filler characteristics are discussed below:

a) particle shape, size and distribution, and degree of agglomeration.
 It is generally accepted that superior filler performance is obtained from fillers having particles not larger than 20 μm. Deterioration of physical properties can occur if particles above this size are present in the filler, and in fact when this is accepted as an upper limit of particle size, then the mean particle size will be in the region of 5 μm.

Coarse filler particles can be responsible for poor surface appearance of mouldings.

For the same volume fraction of filler, irregular shaped particles give rise to an increased degree of agglomeration. This particle interaction facilitates efficient load transfer and results in a higher tensile modulus

[Ahmed and Jones]. The same workers also found that particle size has less effect on tensile modulus than has the degree of agglomeration of particles.

b) Oil absorption

Oil absorption (absorption power) is a function of surface area, fineness and specific gravity of filler particles. Porous particles have higher values than non-porous particles of the same size. The lower the oil absorption, the higher the proportion of filler that can be incorporated. However, highly absorbent fillers may reduce the resin to glass adhesion during curing.

Surface treatment can reduce the oil absorption of a particular filler, thus allowing more filler to be incorporated [Moulson and Mathur].

#### c) Filler packing ratio.

Packing ratio gives a measure of the voidage present in the filler under optimum packing conditions. The denser a filler can be packed, the less binder demand (less interstitial volume) there is at a certain weight percent filler loading, resulting in a viscosity reduction. Greenzweig and Pickering composed an "ideal packing" filler system and confirmed the improved rheological behaviour resulting from such a system [Greenzweig and Pickering].

d) Surface treatment of fillers.

Treating the filler surface can have several advantages:

 higher filler loadings (lower oil absorption) can be obtained while maintaining good flow characteristics.

easier dispersion of fillers.
 Maximum dispersion of filler in resin is imperative to the optimisation and uniformity of every mechanical property of a

compound. Agglomerates and aggregates become stress concentrators, and will be sites where failure originates [Sekutowski].

external stresses can be transferred from the continuous phase to the discontinuous filler phase.

Surface treatment usually consists of the chemical reaction of the mineral surface with a bifunctional coupling agent such as a silane, titanate or zircoaluminate [Cohen]. Separation and stabilisation of filler particles in a liquid matrix can be aided by coating the filler surface with fatty acids such as decanoic acid or stearic acid.

Silane coupling agents have proven to be very successful in improving the mechanical and physical properties of filled systems. Before curing, the coupling agent aids wetting-out and dispersion of filler in resin. Only during cure does the coupling agent bond the filler to the resin [Plueddemann and Stark 1976].

Several workers [Plueddeman and Stark 1977, Canova *et al*] have investigated different ways of applying coupling agents to fillers and their effects on composite properties.

Dispersion of a filler in a liquid polymer involves three steps:

- 1. wetting of filler surface,
- 2. separation of filler particles,
- 3. stabilisation of the dispersion.

Most effective polymer structures for stabilisation are linear chains with polar functional groups spaced widely on the chain. Stable dispersion of filler in the final composite is necessary to eliminate filler agglomerates that would act as weak points for chemical or mechanical failure.

Sometimes coupling agent is confused with sizing. Sizing is the deliberate coating of a filler, for protective purposes, which may incidentally react chemically with the surface. A coupling agent on the other hand always involves a chemical modification that deliberately alters the surface chemistry of a filler.

#### 2.1.2.3 Types of filler

The wide variety of fillers available nowadays makes it difficult to establish a method for classifying these fillers.

One way of organising information on fillers is according to the classification used by mineralogy. About 2000 minerals are recognised as valid species but only a small fraction are used for filler production. Since the 19th century, the classification of fillers has been based on their chemical composition. Minerals are divided into classes depending on the dominant anionic group, e.g. carbonates, oxides, silicates ..., because the anion determines characteristic properties of minerals. After the discovery of X-ray diffraction, it became clear that the internal structure of a mineral should be introduced as a second component of classification. This new element of classification affects mostly silicates, forming the biggest group of minerals. They are divided into subclasses according to their chemical composition and their internal structure [Wypych].

Alternatively, fillers could be classified according to:

- shape (particulate, spherical, flaky, acicular, etc)
- size (particle size range, maximum particle size, etc)
- hardness
- surface treatment
- pH
- surface area
- place of origin.

The most commonly used fillers in moulding compounds are:	
CHINA CLAY:	an aluminium silicate
CALCIUM CARBONATE	
DOLOMITE:	a calcium and magnesium carbonate (a
	carbonate of secondary origin)
NATURAL ORGANIC FILLERS:	woodflour [Wiegand and Unger], alpha
	cellulose, cotton flock, ground peanut and
	walnut shell flour, coconut fibre,
WOLLASTONITE:	calcium oxide and silicate
ALUMINIUM TRIHYDRATE	
MICA:	potassium aluminium silicate
Other fillers are often added in s	mall quantities:
TALC:	magnesium silicate. Talc is the softest
	mineral in the Mohs hardness scale and its
	surface has hydrophobic properties.
FLAME RETARDANTS:	phosphorous, nitrogen, boron and halogen
	compounds.
THICKENING AGENTS:	alkaline earth metal oxides [Gandhi and
	Burns, Fekete], precondensate of resorcinol
	and formaldehyde [Braber and
	Tinkelenberg, Saeki and Tanaka, Sebenik et
	al (1981)]. The thickening agent selected is
	resin specific.
RELEASE AGENTS:	calcium and zinc stearates
LIGHTWEIGHT FILLERS:	hollow glass microspheres, expanded
	vermiculite [Burns, Lynagh and Bradish],
	cork
IMPACT MODIFIERS:	thermoplastic elastomers [Bertolucci]
PHENOL-FORMALDEHYDE WA	STE: ground waste (runners, rejects) [Bauer
	and Redwitz, Weissler].

#### 2.1.2.4 Rheology of filler dispersions

The volume fraction of filler is the main parameter which determines viscosity of resin/filler mixtures. When only a few isolated filler particles are present, resin flow lines have to deviate around the particles and hence will increase viscosity. At higher concentrations, more resistance arises because of interparticle interactions/collisions.

Furthermore, viscosity is influenced by:

- rheological properties of the resin,
- packing ratio: the better the packing efficiency, the lower the viscosity,
- particle shape: increased aspect ratio, i.e. the ratio of length to diameter or thickness, reduces the packing ratio which in its turn increases viscosity,
- particle size: the smaller the average size the higher the viscosity.
- filler surface properties: roughness and irregularities increase viscosity.
- temperature and pressure: an increase in temperature and/or a decrease in pressure cause an increase in the maximum packing ability and thus results in a lower viscosity.

#### 2.1.3 Fibre Reinforcement

#### 2.1.3.1 Introduction

Reinforcements are materials added to increase the modulus and/or strength of a compound. This definition makes it difficult to distinguish between reinforcing fillers and fibrous reinforcements. However, one way of separating fibre reinforcements from other additives is the fact that reinforcements all offer high specific modulus and strength.

Typically, properties affected by reinforcement include an increase in impact resistance, tensile strength, flexural strength and modulus and compressive strength and a decrease in shrinkage and the thermal coefficient of expansion. As a rule of thumb, the modulus of a fibre should be at least ten times that of the matrix before any significant reinforcement is achieved.

#### 2.1.3.2 Types of fibre reinforcement

Many fibres are currently being used to reinforce phenolic resin. Each offers their unique set of properties as a reinforcement.

#### GLASS FIBRE

One of the most extensively used reinforcements in engineering phenolics is glass fibres. Glass fibre as a low cost reinforcement offers many advantages including high tensile strength, high degree of elasticity, outstanding dimensional stability, low thermal and electrical conduction, low elongation, high temperature resistance, resistance to most corrosive chemicals, excellent moisture resistance and a hard impervious surface which is mildew and rot resistant [Lubin]. Several types of glass fibre are available, but the type predominantly used is the type E glass fibre which is a low-alkali borosilicate [Parkin].

#### CARBON FIBRE

As a reinforcing fibre in phenolic moulding compounds, carbon fibres offer distinctively different engineering properties compared to glass fibre reinforcement. Greater stiffness at a reduced density as well as electrical and thermal conductivity are advantages of using carbon fibre materials. The main disadvantage however is the cost of carbon fibre in comparison to glass fibre.

#### ARAMID FIBRE

Aramid fibres offer an excellent specific strength and stiffness. Reduced fire performance and a poor compressive strength are the drawbacks.

#### SILICA FIBRE

Silica fibres are used as a reinforcement in phenolic resins in ablative applications; because of their superior thermal resistance [Rossa].

#### **OTHERS**

A wide range of fibres are being used in specialty applications and a variety of matrix types. These include boron, ceramic, calcium sulphate, magnesium and calcium silicate fibres.

#### 2.1.3.3 Fibre sizing

An important requirement of glass fibre reinforced composites is good adhesion between the glass and the matrix. The adhesion must be strong and not significantly weakened by environmental conditions to which the part may be exposed. If adhesion is weak or weakened by the environment, stresses will not be effectively transferred from fibre to fibre, and optimum reinforcing action of the fibres will not be realised. Good adhesion is obtained by the application of coupling agents which react with or bond strongly to both the glass fibre surface and the matrix. Coupling agents are usually applied to fibres in the form of an aqueous-based size. Sizes are chemically diverse and complex mixtures of film-forming polymers and coupling agents. The film-forming polymers are formulated to wet-spread to form a uniform coating that is applied to protect the reinforcement during processing.

Sizes are applied to the fibres as they are formed. The functions of a size are the following:

- to adhere the fibres together to protect the normally brittle glass from abrasion,
- to lubricate fibres in subsequent processing,
- to impart antistatic properties to the fibre,
- to provide a good chemical bond to the glass fibre surface and the matrix which it will eventually reinforce.

Sizings may be a "necessary evil" in that they are needed in one stage of processing but interfere with subsequent processing and/or adversely affect composite mechanical properties. Usually, sizes are present on the glass fibre in quantities of approximately 1% by weight or less.

The use of sizings as protective coatings is largely empirical, with relatively little documentation. In distinct contrast to the film-forming sizings, the adhesion promoters - especially the silanes - have been extensively studied. The reason for this interest is primarily that these agents do in fact improve the moisture resistance of glass fibre reinforced polymer composites. However, despite all the studies of silanes on glass (and other) surfaces, the mechanisms involved in their protection of the glass-polymer interface are not well understood.

The early concept of the silanes forming a simple chemical coupling between fibre and matrix (Figure 2.2) has been largely discredited. The silanes readily form three-dimensional polysiloxane networks through hydrolysis and condensation of the alkoxy groups (Figure 2.3). It has been suggested that this is a relatively open network that is easily penetrated by the molecules of the matrix polymer so that an entanglement of the polymer networks is formed in the interphase region between matrix and reinforcement (Figure 2.4) [Composites].



### FIGURE 2.2:

Idealised "coupling" of matrix and glass by organofunctional silane.



FIGURE 2.3:

Hydrolysis of organofunctional silanes to polysiloxane networks.



FIGURE 2.4: Silane and matrix interphase polymer network.

In general, silanes that are effective in glass fibre reinforced composites are also preferred in particulate mineral filled composites. Amino-functional silanes are used for phenolic resin composites.

The wet resin and cured compatibility of glass fibre/acid cure phenolic resin composites has been extensively studied [Tavakoli *et al* (1989), Tavakoli *et al* (1990)] using contact angle measurements, differential scanning calorimetry and

interlaminar shear strength measurements. Chang and co-workers found that sizings on carbon fibre reinforced phenolic resins do not have any significant effect on the mechanical properties [Chang *et al*].

#### 2.2 PHENOLIC MOULDING COMPOUNDS

Standard specifications for phenolic compounds and phenolic moulding compounds are described in ASTM D4617 and D700 respectively. Compounds are classified into groups according to their application (ASTM D4617) or their characteristics (ASTM D700).

Phenolic moulding compounds exhibit the following key properties:

- high temperature resistance,
- modulus retention at high temperature,
- flame and arc resistance,
- resistance to most chemicals,
- high surface hardness,
- good electrical properties,
- relatively low cost [Knop and Pilato].

Based on these key features, they are used within a wide spectrum of applications. The high working temperature and relatively poor thermal conductivity of phenolic FRP has ensured the material many under-the-bonnet applications such as: distributor caps, fuse blocks, connectors and brake components. Mass transit applications such as in airports, undergrounds and railways are finding phenolic FRP the most suitable material. Ventilation ducting, methane drainage pipes, seats and applications in the Channel Tunnel use phenolic FRP.

The construction industry makes use of phenolic FRP in public structures where large numbers of people congregate and in buildings where escape may be difficult for various reasons. There are numerous applications in electrical equipment and even the interiors of leisure submarines have been fitted with phenolic FRP [Hunter and Forsdyke].

#### 2.3 COMPOUNDING OF DOUGH MOULDING COMPOUNDS

In order to produce DMC's, thermosetting resins are compounded with various additives including fillers, reinforcements, pigments, release agents, etc... Either batch mixers like sigma blade (or Z-blade) mixers and mixing rolls, or continuous mixers like twin screw extruders and continuous kneaders may be utilised for such compounding.

The rheological material functions, the processability behaviour, and the ultimate properties of articles processed from the thermosetting compound depend strongly on the thermomechanical history experienced by the resin during the compounding stage. Premature curing of the compound adversely affects its flow, curing and processability [Kalyon and Hallouch]. One key factor in maintaining optimum strength properties is the minimisation of glass fibre damage.

#### **Batch Mixing**

Originally, compounding was done by feeding the compound components to mixing rolls. The blankets of compound produced were cooled, crushed and ground. This process is successful for formulations containing abrasive fillers or small production quantities [Knop and Pilato]. High-speed mixers, using combinations of heating and cooling mixers, have been employed to compound powdered novolak resins with a wide range of fillers and fibres [Bornemann].
#### Chapter 2: Literature Survey

Nowadays, one of the most common compounding methods is the use of the sigma blade mixer. In this method, resin matrix in a liquid form is first mixed with filler(s) in order to fully wet out the filler particles. Subsequently, chopped fibre reinforcement (typically 3, 6 or 12 mm long) is charged to the mixer and mixing continues for a further 10 to 15 mins after which time the dough can be further consolidated by means of an extruder into a rope. In the case of polyester moulding compounds, the resin is usually premixed with thermoplastic additive, styrene momomer (if required), organic peroxide catalyst, internal release agent, pigments and inert fillers. This resin mix is often prepared in a variable speed, high-shear, single-shaft mixer known as a dissolver or disperser. Subsequently, the resin mix is dumped into a double arm high intensity mixer for the production of dough moulding compounds, or pumped to a continuous mixer for the preparation of sheet moulding compounds. If the mix is to be thickened, the chemical thickener is added at that point. In the case of dough moulding compounds, the glass fibre reinforcement is then added during a controlled mixing cycle [Composites].

These processes for the manufacture of DMC intrinsically degrade glass fibres. Fibres are broken down into single filaments, and the resultant monofilaments are fractured into elements of lower aspect ratio. Mixing time has been found to be critical in determining the glass fibre length degradation [Burns]. Mixing time adversely affects flexural, tensile and particularly impact properties. Questions of workplace hygiene, labour costs, energy consumption, uniformity and reproducibility of quality are decisive in the development of continuously operating compounding installations.

#### Continuous Compounding

The production of moulding compounds in extruders offers economical, dustfree and odour-free processing and efficient homogenising. Thermosets have been compounded using continuous kneaders [Waelty, Kalyon and Hallouch]. Single screw continuous kneaders are characterised by a kneading screw which rotates and oscillates in a barrel. Dispersion and homogenisation takes place in between the rotating and oscillating screw flights and the kneading teeth. Waelty describes the production of polyester DMC using Buss Ko-Kneaders. Resin and a mixture of fillers are homogenised in the first kneader zone. In the second kneader zone, 12 mm long chopped glass fibre strands are blended into the resin compound. A screw picks up the finished DMC and forms it into a round "rope" by means of a die. Work by Kalyon and Hallouch shows that the selection of operating conditions for a given formulation such as feeding screw speed, kneading screw speed and barrel temperature is very critical, as only stable conditions during compounding can generate compounds with acceptable processability and quality.

Co-rotating twin screw extruders are used for the compounding of thermoplastics with chopped glass fibres. Generally, glass strands enter via a side feeder into a homogeneous polymer melt. A second mixing stage is then used to incorporate the glass into the polymer. The composite variables most influenced by process design and operating parameters include average glass fibre aspect ratio, the amount of low end fibre lengths (fines) and coupling at the interface of the glass surface and the polymer. In general, optimisation of these process related composite properties involves attainment of maximum fibre lengths, minimal number of fines which tend to act as a brittle filler rather than a reinforcement, and maximum chemical coupling at the polymer-glass fibre interface. There are three mechanisms by which fibre breakage can occur during extrusion:

- fibre-fibre interaction. This can occur due to abrasion or bending by
   fibre overlap
- fibre contact with processor surfaces which is evident from wear in compounding equipment used with glass fibres

 fibre interactions with the polymer. Viscous loading by the polymer results in compression, or more likely fibre bending.

Reduction in fibre breakage and reduced amounts of fines occur with gentle mixing while chemical coupling is optimised by the continuous unbundling of glass fibre strands to achieve complete exposure of glass surface area, this being accomplished by intensive distributive mixing [Grillo *et al*]. So, it is important to define a operating window in which the correct balance is struck between fibre length and the strength of the fibre-polymer bond. Work carried out by a manufacturer of twin screw extruders [Wall, Swanborough] has shown that the length of the mixing section has the most significant effect on both parameters. As the mixing length increases, the fibre length will decrease, while the fibre matrix bond will, up to a point, improve.

The same rules or principles are valid when thermosets are compounded with fillers and fibres. However, compounding is carried out at much lower temperatures in order to prevent premature curing of the resin. Therefore, especially in the case of highly filled systems, cooling rather than heating of the barrel is applied as substantial amounts of shear heat can be released.

Compounding phenolic resol resin with filler and continuous glass fibre roving, rather than chopped glass fibre strands, has several advantages [Kazemi, Kazemi *et al*]. The careful choice of both screw configuration and the insertion point along the barrel of the glass fibre roving affects the average glass fibre length, which in turn determines flexural and impact properties. Using this process, DMC can be produced with an average glass fibre length several times larger than that found in traditional DMC's. This results in long fibre DMC having superior mechanical properties.

## 2.4 PROCESSING OF DOUGH MOULDING COMPOUNDS

Moulding compounds can be processed by compression, transfer, or injection moulding. All three techniques involve material flow in the mould.

#### **Compression Moulding**

The compression moulding process yields stronger mouldings than either transfer or injection moulding processes. Since material flow is relatively low, there is no fibre orientation or fibre attrition. Curing time is relatively long, i.e. approximately 1 min per mm thickness [Chevalier].

The main disadvantage is the low level of automation of the conventional compression moulding process. Automated press loading systems and preplasticators have been developed with the aim of reducing the cycle time by preheating the charge and reducing the operator input. As a result of the low level of automation, a wide variation in mechanical properties of mouldings produced by compression moulding exist. Charge geometry, closure speed of the press, moulding pressure, press dwell time and moulding temperature all affect the final properties of a moulding [Farouk and Kwon, Hunkar, Burns *et al*].

#### **Transfer Moulding**

In the transfer moulding process, preformed, portioned and preheated material is pressed from a heated transfer chamber by a plunger through a gate into the closed mould. The compound is preheated in the transfer chamber and, in addition, frictional heat is transferred during the flow through the narrow gate. This results in shorter curing times and more homogeneous crosslinking compared to compression moulded samples. Compounds containing only relatively short fibres can be processed and a certain degree of fibre orientation is unavoidable [Knop and Pilato, Owen *et al*].

## **Injection Moulding**

The injection moulding process requires materials capable of being fed into a moulding machine, transported to accumulate pressure, injected through channels, and made to flow into a small opening in the mould. The process may cause major changes in both the physical and chemical properties of the moulding compound. Consequently, parts produced from moulding compounds represent a compromise between optimum physical properties and the essential ability to flow under pressure [Composites]. Therefore, compounds containing fibres longer than 25 mm will most probably encounter flow problems [Gibson and Payne]. A typical injection compound has a higher resin content and a higher internal lubricant content than a compression compound, and therefore has a longer flow path.

The injection moulding process gives fast cycle times, improved surface finish, greater consistency, closer dimensional tolerances, and lower handling and finishing costs [Pennington and Shortall]. The main disadvantages are fibre degradation which can result in loss of strength and impact resistance, and fibre orientation [Gibson].

The amount of fibre degradation is related to the work done per unit volume of material processed. Careful design of the screw, die and mould, and alternative refill procedures reduce the processing work, and subsequently improve the mechanical properties [Williamson *et al*].

Another moulding technique currently gaining acceptance is a combined injection/compression moulding process. A full shot of material is injected into a partially closed mould. The mould is then closed at full clamping pressure which forces the material to fill the mould cavity. This technique combines the advantages of the compression and injection moulding processes.

# CHAPTER III EXPERIMENTAL

#### 3.1 MATERIALS

Phenolic dough moulding compounds consist of phenolic resin, filler(s) and glass fibres. These materials will hereafter be referred to as "compounds". Resin/filler mixtures without glass fibres will be known as "mixtures".

#### 3.1.1 Phenolic Resins

The two phenolic resol resins Cellobond J2027L and Cellobond J2040L have been investigated as potential matrices: both resins are supplied by BP Chemicals Ltd. Cellobond J2027L is a resol resin that is specifically designed for fibre reinforced plastics. This resin is essentially an acid-cure system, but curing is also possible at elevated temperatures without the addition of a catalyst. The higher the temperature, the faster the curing reaction will proceed. The Cellobond J2040L resol resin on the other hand is a heat cure system which is primarily used as a binder resin for ablative applications.

These two resins were chosen for this work for different reasons. First, the low viscosity resin J2027L is a well-established phenolic resin in the Fibre Reinforced Plastics (FRP) industry. In FRP applications, its low viscosity allows good wetting of the glass fibres. The resin can be cured by both acid curing and heat curing. Second, the high viscosity resin J2040L was chosen as it is crucial to maintain a certain level of viscosity during the compression moulding of dough moulding compounds in order to prevent resin/filler washing-out, resulting in excessive amounts of flash. Table 3.1 gives detailed specifications of the resins.

Property	J2040L	J2027L
Solids content at 135°C (%)	71.5-75.5	±65
Free phenol (%)	7	7-8
Free formaldehyde (%)	1	2-3
pH	8.6-8.8	7.3-7.8
Specific gravity at 25°C	1.260±0.005	1.225±0.005
Viscosity at 25°C (in Pa.s)	7.000	250-300
Water content (%)	4-5	10-13

## TABLE 3.1: Phenolic Resin Properties

#### 3.1.2 Fillers

A wide range of minerals have been investigated as potential fillers for phenolic dough moulding compounds, with pH and particle size (distribution) being the prime factors in selection.

It was decided to investigate inorganic fillers only (with the exception of the clay/cellulose mixtures), in order not to jeopardise the fire performance of the moulding compounds.

#### 3.1.2.1 China clays

The following grades of china clay have been investigated: Polarite 102A, PoleStar 200R and Devolite. These fillers were chosen in order to study the effect of particle size (Devolite versus PoleStar 200R) and coupling agent (Polarite 102A versus PoleStar 200R). The fillers were supplied by ECC International Ltd. In Table 3.2 coupling agent, pH, surface area and average particle size are given for the aforementioned china clays.

Filler Tradename	Filler surface	рН	Surface area (m²/g)	Average particle size (μm)
Devolite	Uncoated	7-8	7	3
PoleStar 200R	Uncoated	6-7	8.5	1.8
Polarite 102A	Silane coated (A1100)	8.5-10	8.5	1.8

TABLE 3.2: Characteristics of China Clays

Note: A1100 =  $\gamma$ -aminopropyltriethoxysilane Moh's hardness = 4 Density = 2.6 g/cm<sup>3</sup>

## 3.1.2.2 Calcium carbonates

Four different grades of calcium carbonate have been evaluated.

Albarex, Britomya V and Omya BL were supplied by Croxton and Garry Ltd. These calcium carbonates were chosen as they allowed a comparison to be made between two uncoated fillers with different average particle sizes (Britomya V and Omya BL) on the one hand and two fillers with the same average particle size but one is surface coated while the other one has an uncoated surface (Albarex and Omya BL) on the other hand.

The fourth calcium carbonate investigated was Polarite 420EW, which is supplied by ECC International Ltd. The main physical characteristics of these fillers are given in Table 3.3. The supplier of Polarite 420EW would not disclose the type of polymeric coating that is applied to the filler.

Filler Tradename	Filler surface	Absorption (g/100g)		Density (g/cm³)	Average particle	
		Oil DOP				
Polarite 420EW	Polymeric coating and pigment	-	-	2.5	3	
Albarex	Fatty acid (calcite)	14	15	2.7	5	
Omya BL	Uncoated (calcite)	16	25	2.7	5	

 TABLE 3.3:
 Characteristics of Calcium Carbonates

#### 3.1.2.3 Other fillers

The following fillers were introduced as primary and/or secondary fillers: dolomite, aluminium trihydrate (ATH), wollastonite, mica and clay/cellulose mixtures. Table 3.4 gives more information regarding these fillers. Dolomite is widely used in polyester moulding compounds and particulate filled epoxy systems. This particular grade (Microdol H400) is recommended for moulding compound applications and was also chosen because of its low surface area and large average particle size. ATH is used as a fire retardant in thermoplastic and thermosetting systems. The filler decomposes from 200°C onwards into aluminum oxide and water. The released water reduces the temperature and consequently slows the burning process down. Wollastonite is an acicular filler with a high hardness which is often used as a reinforcing agent. Mica is a flaky filler with a relatively low pH. Its flaky nature often results in good flexural properties. In phenolic moulding compounds, woodflour is the most widely used filler. In this work, woodflour was not studied in great detail as it was expected that the organic nature of the filler would result in a deterioration of the fire performance of the compound. Clay/cellulose filler mixtures were investigated for completeness and in order to be able to compare the compounds with mineral filled systems.

#### 3.1.2.4 Release agents

Very poor release properties of compounds containing phenolic resin necessitated the use of external and internal release agents. The effects of several internal release agents on the release and flexural properties of resin/filler mixtures were investigated.

#### a) External release agent

The external release agent used in this work was Frekote 700NC, supplied by Rotec Chemicals. This release agent consists of a polymeric resin, dissolved in a mixture of aliphatic petroleum distillates and dibutyl ether. The supplier was

Filler	Tradename	Chemical Composition	Hardness	Density	рН	Abs (g/	Absorption (g/100g)		Average particle size
				(g/cm³)		Oil	DOP	(m²/g)	(μm)
Dolomite ATH Wolłastonite Mica	Microdol H400 <sup>(1)</sup> Trihyde ON4608 <sup>(2)</sup> Vansil EW-20 <sup>(3)</sup> FDP/4 <sup>(3)</sup>	CaMg $(CO_3)^2$ Al $(OH)_3$ CaSiO <sub>3</sub> SiO <sub>2</sub> Al <sub>2</sub> O <sub>3</sub> K <sub>2</sub> O	3.5 - 4.5 2.5	2.85 2.4 2.9 2.8	10 8-10 9.8 7-9	15.5 27.0 20.0	37.0	0.9 - 2.4 -	13 - -
Clay cellulose 70/30 30/70	F-STEND 10 <sup>(4)</sup> F-STEND K2 <sup>(4)</sup>	Cellulose and a mixture of china clay and calcium carbonate	-	-,	7-7.5	-	-	-	90%<10 μm 50%<50 μm

TABLE 3.4: Characteristics of Other Fillers

The fillers were supplied by:

- 1.
- 2.
- Norwegian Talc Minerals AS Croxton and Garry Ltd Microfine Minerals and Chemicals Ltd 3.
- Fosse Ltd 4.

not prepared to disclose details regarding the nature of the polymeric resin. This solution was applied to a cleaned metal surface using a dust-free, clean cotton cloth. The solvents were allowed to evaporate, leaving the polymeric resin behind. The polymeric resin is subsequently cured on to the metal surface, forming a weak boundary layer, thus aiding demoulding.

#### b) Internal release agents

Six different types of internal release agent have been investigated (see Table 3.5).

Additive	Supplier
PAT 660/K PAT 664/A PAT 659/B TR016 Mold Wiz INT-1854 Mold Wiz INT-1858	E. und P Würtz GmbH and CoKG " Schill and Seilacher Axel Plastics Research Laboratories Inc

<b>FABLE 3.5:</b>	Internal	Release	Agents
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#### 3.1.3 Glass Fibres

Three types of glass fibre were investigated as potential reinforcements in phenolic moulding compounds: Vetrotex P223, Owens-Corning R52 and Silenka 087. These glass fibres are all coated with silane coupling agents and have a linear density of 2400 Tex. Further information is given in Table 3.6. Both Vetrotex P223 and Owens-Corning R52 glass fibres are designed specifically for unsaturated polyester resin systems, but their sizes have different degrees of solubility in styrene. The Silenka 087 glass fibre surface coating was developed for thermoplastic materials such as polyamides, rather than polyester resins.

Glass fibre	Strand tex (g/km)	Fibre diameter (µm)	Size content (%)	Glass fibre bundle solubility in polyester resin systems
Vetrotex P223	25	11	0.67	High
Owens-Corning R52	67	-	-	Low
Silenka 087	126	10	1	Very low

TABLE 3.6: Glass Fibres Characteristics

#### 3.2 COMPOUNDING OF MATERIALS

Phenolic resin and filler(s) were compounded using two different techniques: a batch process, i.e. Z-blade mixer, and a continuous process, i.e. twin screw extruder. The majority of the resin/filler mixtures were prepared using the twin screw extruder. However, in some cases extra resin/filler mixtures were prepared using the Z-blade mixer when it was necessary to investigate a wider filler loading range. This batch process is a more efficient way of mixing resin and filler when only a few compounds at a time are produced. Preliminary trials indicated no differences in properties between samples prepared using either the batch or the continuous mixing processes. No dough moulding compounds were produced using the Z-blade mixer: only the twin screw extruder technique was employed for the incorporation of glass fibre.

#### 3.2.1 Z-blade mixer

In this study, a laboratory scale Baker Perkins Z-blade mixer was used. The mixer had sigma type blades and a volume capacity of 2 litres. The following settings were used:

- speed ratio between the blades: 1: 3
- blade rotating speed: 60 rpm (fast blade)
- mixing temperature: 30°C
- mixing time: 20 mins.

The experimental procedure is as follows:

- 1. Introduce the resin.
- Rotate the blades for 5 minutes at 60 rpm in order to preheat the resin to 30°C.
- 3. Add the filler over a 1-3 minute span.
- 4. After a few minutes, stop the mixer and scrape filler and resin/filler slurry off the mixer walls, back into the mixer.
- 5. Continue mixing for a total of 20 minutes of mixing.
- 6. Stop mixer.
- 7. Discharge.

The mixtures are placed in polyethylene bags and stored in a freezer until required for characterisation (viscosity and burn-off tests) and subsequent processing. The total weight of a batch was approximately 1800g.

#### 3.2.2 Twin Screw Compounding

#### 3.2.2.1 Ancillary processes and equipment

Due to the small amount of internal release agent that was added to the compound, i.e. 2 parts per 100 parts of filler, it was decided to premix the internal release agent with the filler, prior to the twin screw compounding process. The filler was mixed with the internal release agent (TR016) in a double cone mixer. The mixer, manufactured by Neco, was of the type GAP.ST.FG, size 10". The rotational speed was 40 rpm, and mixing continued for 5 minutes.

The filler/internal release agent mixture was transferred to a feed hopper. Different fillers were mixed separately with the internal release agent and placed in different hoppers, so that changes in filler combinations could be carried out quickly, without the need for recalibrating the feed hoppers. The two feed hoppers that were used were of the K-Tron T20 type, with twin screw feeders and vertical agitators in order to reduce the filler bridging tendency.

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In order to feed the resin into the twin screw extruder, a pump capable of metering small amounts (up to 70 g/min) of high viscosity resin was required.

After several pumps had been tried unsuccessfully, a HB Consultants QM100P peristaltic pump with a 7018 pumphead and marprene tubing was acquired. As the viscosity of the resin was so high and very temperature sensitive it was found necessary to preheat the resin to 30°C. This allowed the resin to be pumped at the required rate.

#### 3.2.2.2 Main set-up

The majority of the resin/filler mixtures and all the moulding compounds were prepared on a co-rotating intermeshing twin screw extruder. The equipment used was an APV MP2030 LAB machine. Figure 3.1 shows the set-up used for the production of moulding compounds. Resin and filler were introduced in the same port upstream along the extruder. Glass fibres were added further downstream, in the final feedport just before the diehead.

Resin/filler mixtures were prepared in the same way, with the exception of the introduction of glass fibres. The screw configuration that was used for the mixtures and compounds is shown in Figure 3.2. The barrel temperature was set at 50°C, with the exception when the effect of barrel temperature was being investigated. Torque, expressed as a percentage, was recorded and indicates the energy required by the extruder during compounding. Torque is an indirect measure of viscosity.

Glass fibres were introduced into the filled extruder using the pulling force of the rotating screws. The higher the screw speed, the greater the amount of glass fibres that were introduced. A calibration curve of glass fibre intake (per unit weight) versus extruder screw speed could then be determined. During compounding, it was found necessary to vary screw speed in order to incorporate the desired amount of glass fibre. In order to maintain long fibre lengths in the compounds, it was necessary to minimise the flow restrictions

## Chapter 3: Experimental



## LEGEND:

- 1. Temperature controller
- 2. Waterbath
- 3. Phenolic resin
- 4. Peristaltic pump
- 5. Motor assembly
- 6. Filler hopper

- 7. Feed port (resin and filler)
- 8. Feed port (glass fibre)
- 9. Glass fibre continuous roving
- 10. Screw
- 11. Diehead
- 12. Barrel

## FIGURE 3.1:

Schematic diagram of the set-up used for compounding phenolic moulding compounds

within the extruder experienced by the material, which would otherwise reduce the glass fibre length. Therefore, the compounds were extruded directly out of the diehead, without passage through a die. No haul-off unit was used when the moulding compounds were discharged. Instead, the extrudates were discharged directly into polyethylene bags and stored in a freezer. Tables 3.7 and 3.8 show the resin/filler mixtures that were prepared using both the batch and continuous processes.



#### FIGURE 3.2: Screw configuration used for compounding moulding compounds

Tables 3.9 and 3.10 show the resin/filler/glass fibre moulding compounds that were prepared using a twin screw compounder. In Table 3.9, glass fibre content is expressed in a weight percentage (wt %) of the total weight. Filler loading is expressed in parts per hundred parts of resin (phr). An alternative way to describe different compositions (see Table 3.10) is by representing a compound in the following way:

wt % resin / wt % filler / wt % glass fibre

*Example:* A 40/40/20 compound contains 20 wt % glass fibre and 40 wt % of both resin and filler, or 100 phr of filler.

Loading (phr)	Polarite 102A/dolomite				Devolite/dolomite		PoleStar 200R/dolomite		Dolomite	
	100/0	70/30	50/50	30/ <b>70</b>	100/0	50/50	100/0	50/50	-	
40	x		-							
46		X		1						
49			X	ł						
52 57									v	
57	^			j	v				X	
59					<b>^</b>		Y			
66		x								
69		, n								
71				X					x	
75			X		X					
76				ļ		Х				
77							X			
79				]				X	Х	
80	Х			· ·						
83					X					
86		<b>v</b>		!					v	
88									X	
92				<b>^</b>			Y Y			
94			x		x					
96	x			}						
97						х				
100		X								
104								x		
110				<b> </b> ,	X					
111				Х						
112				ĺ		X				
113	X						×			
116	ļ			ļ	ļ		l			
119							1		X	
120									^	
131	ļ								x	
134				x						
135	1	Í		1			1	}		
147										
148		X					1			

TABLE 3.7:	Resin/filler	mixtures	that	were	prepared,	containing	china	clay,
	dolomite ar	nd mixture	es of	both	fillers	-		-

TABLE 3.8:	Resin/filler	mixtures	that	were	prepared,	containing	resin	and	either	а
	calcium cat	rbonate, A	ATH o	or woll	astonite					

Filler											
Loading (phr)	Calcium Carbonates				PoleStar	200R/ATH	<b>i</b>	Polarite 102A/Wollastonite			
	Albarex	Britomya	Omya	Polarite 420EW	100/0	70/30	50/50	30/70	100/0	80/20	60/40
40 57 62 77 80 94 96 131 155 170 172 179 181 190 194 202 204 243 252 272 291 296	x x x	x x	××	X	x x x x x	×	x	x	X X X X	x	×
202 204 243 252 272 291 296 333	X	x	X X	x x x			x	x			

Filler	Glass fibre content (wt %)											
loading (phr)	10	15	20	25	30	35	40					
40 60 80 100 120 140 160 200	X X O	X X X X X X X X X	X X X X X X X X	X X X X X X X X X	X X X X X X X X X	X X	O X					

TABLE 3.9:	Composition window:	moulding	compounds	that were	prepared
	using a twin screw ext	truder			

Legend:

X: 0

Compounds that were prepared Compounds that could not be prepared

Both methods can be used. However, for comparative purposes, the former method (see Table 3.9) is more user friendly and is therefore used throughout this work.

For completeness Table 3.10 illustrates the alternative method for expressing the moulding compound compositions shown in Table 3.9.

Tables 3.11 and 3.12 show the moulding compounds that were prepared using different types of glass fibres and fillers.

The moulding compounds that were prepared in order to study the effect of extruder output rate are shown in Table 3.13.

 TABLE 3.10:
 Composition window: moulding compound compositions expressed in weight percentages

Resin:J2040LFiller:Polarite 102AGlass fibre:Owens-Corning R52

wt % resin / wt % filler / wt % glass fibre

Filler loading (phr)	Glass fibre content (wt %)						
	10	15	20	25	30	35	40
40		61/24/15	57/23/30	59/21/25	50/20/30		
60	56/34/10	53/32/15	50/30/20	47/28/25	44/26/30	41/24/35	
80		47/38/15	44.5/35.5/20	42/33/25	39/31/30		
100	45/45/10	42.5/42.5/15	40/40/20	37.5/37.5/25	35/35/30	32.5/32.5/35	30/30/40
120		39/46/15	36/44/20	34/41/25	32/35/30		
140		35/50/15	33/47/20	31/44/25	29/41/30		
160		33/52/15	31/49/20	29/46/25	27/43/30		
200		28/57/15	27/53/20	25/50/25	23/47/30	<u> </u>	

TABLE 3.11:Overview of the compounds that were prepared using<br/>different types of glass fibres:

Resin: J2040L Filler: Polarite 102A Glass fibres: Either Vetrotex P223 or Silenka 087

Filler Loading (phr)	Glass fibre content (wt %)			
	10	20	30	40
60	x	X	X	0
100	Х	X	X	X
140	0	X	X	

Legend: X: Compounds that were prepared

O: Compounds that could not be prepared

TABLE 3.12:Overview of the compounds that were prepared using<br/>different types of filler:

Resin:	J2040L
Filler:	Polarite 102A/Mica 50/50
	Mica
	Clay/cellulose 70/30
	Clay/cellulose 30/70
Glass fibre:	Owens-Corning R52

Filler Loading (phr)	Glass fibre content (wt %)				
	20		15		
	Polarite/Mica		Clay/Cellulose		
	50/50	0/100	70/30	30/70	
20 40 60 100 140	X X X	X X X	X X X	X X X	

# TABLE 3.13: Compositions that were prepared in order to study the effect of extruder output rate

Extruder Output (g/min)	
100	Х
125	X
150	X

#### 3.3 CHARACTERISATION OF UNCURED MIXTURES AND COMPOUNDS

#### 3.3.1 Determination of Composition

Burn-off tests were carried out on mixtures and compounds in order to determine the ignition loss of these materials. Preliminary trials indicated that when pure phenolic resin was burned-off (following the procedure outlined below), complete decomposition of the resin to volatile materials occurred. Similar tests on pure fillers were carried out in order to detect any losses of volatiles such as water of crystallisation. The necessary adjustments were made in the cases where weight losses did occur, so that ignition loss results could be converted in resin content data.

The accurately weighed specimens, weighing in the range of 5 to 6 g, were put in a crucible and kept in a furnace at 600°C for 4 hrs. Trials had indicated that a burn-off time of 4 hrs at a temperature of 600°C resulted in complete polymer loss. After cooling down, the samples were reweighed and the resin content was calculated.

#### 3.3.2 Viscosity Measurements

The viscosities of resin/filler mixtures were measured using a Haake RV2 viscometer fitted with the PK (cone and plate) sensor system. The angle between the cone and plate was 1°. The sample was squeezed out between the cone and plate by means of a spring which presses the plate up against the

cone. Different types of spring strength are available and were used accordingly, depending on the viscosity of the mixture.

The viscosities of phenolic resin at different temperatures and mixtures of different phenolic resins were determined using the Haake RV2 viscometer with a Couette sensor system. The greater contact area between the two parallel cylinders allowed a more accurate reading of viscosity for relatively low viscosity materials.

#### 3.4 CURING

Two different curing techniques were employed, depending on whether mixtures or compounds were involved, i.e. a casting technique and the compression moulding process.

#### 3.4.1 Casting

It was found impossible to produce acceptable cured samples of resin/filler mixtures by compression moulding. Before the curing process was initiated, the decrease in viscosity due to heating resulted in excessive material flow and consequently the mould could not retain the mixture. Therefore, it was decided to cast resin/filler mixtures instead of compression moulding them. This technique was suggested by BP Chemicals.

In order to optimise the casting process, several casting temperatures were investigated. It was found that casting at an oven temperature of 85°C resulted in satisfactory samples. Any oven temperature higher than 85°C resulted in blistering. When casting pure resin (J2040L), it was found that the presence of bubbles in the sample was greatly reduced when, prior to casting, the resin was put in a vacuum oven at 60°C for 1 hour. The same procedure, when applied to filled samples, resulted in an inferior surface finish.

#### Chapter 3: Experimental

The casting method evolved was as follows: uncured resin/filler mixture was put in a cold compression mould. Low pressure was applied at room temperature, just sufficient for the sample to flow and fill the mould cavity. "Compression moulding" the mixture, resulted in a sample of fixed dimensions, i.e. constant thickness. The uncured sample was then carefully removed from the mould and placed between two glass plates. Subsequently, the sample was cured in an oven at 85°C for 6 hrs. Most samples (except the Polarite 102A containing samples - see above) maintained their original compression moulded shape. The cured samples where then removed and allowed to cool down. A weight of approximately 5 kg was put on top of the cooling samples, to prevent warping.

Cooling samples shrink, and it is this shrinkage which causes warpage. Mixtures containing higher filler loadings shrink less, resulting in a reduced tendency to warping. However, this procedure was not applied to Polarite 102A containing mixtures. At 85°C the viscosity of these mixtures decreased substantially so that the samples could no longer be contained between the glass plates. The breakdown of the hydrogen bonds between the aminosilane coating of the filler and the phenolic resin at 85°C could explain this decrease in viscosity. Therefore, the samples were cured in a tray. After 75 minutes, the castings were subjected to slight pressure in a compression mould in order to obtain a flat surface, free of holes or bubbles. The samples were then allowed to fully cure under a weight of approximately 1 kg. After a total curing time of 6 hrs, the samples were removed and cooled in the same manner as the other samples.

Both casting techniques resulted in samples with an identical curing history and a thickness of 6-7 mm.

#### 3.4.2 Compression Moulding

Dough moulding compounds were compression moulded using a hand operated hydraulic press. A positive flash mould, resulting in mouldings of 130 x 45 mm<sup>2</sup>, was sandblasted, cleaned and chrome-plated. After degreasing the mould with acetone, the external release agent was applied and cured on to the metal surface. This final step was repeated at intervals as the release agent coating wears off. On average, external release agent was re-applied after approximately five moulding cycles.

Sufficient amount of material for the manufacture of a moulding was taken and rolled into a ball-shaped dough in order to randomise any fibre orientation that may exist in the moulding compound. This "precharge" was hot pressed between two metal plates, in order to obtain a flat shape. This plaque of material was rolled into a cylindrical shape, roughly the size of the mould, and preheated in a 750W microwave oven for 75 secs. This was done in order to remove some of the volatiles present in the compound and to improve the material flow in the mould which in turn reduces the amount of damage to the glass fibres. The latter two steps: hot pressing into a flat shape and rolling the material into a cylindrical shape further ensured isotropic properties of the cured compound. No evidence of anisotropy was observed during mechanical testing. The material was then introduced into the cold mould and pressed at 190°C. Better results were obtained when the material was placed in a cold rather than a hot mould. In a hot mould, resin/filler slurry flowed immediately after the moulding compound was introduced. The glass fibres remained in place. This "washing-out" effect of slurry was not seen when the compound was introduced in a cold mould. Previous work carried out by Kazemi showed that a moulding temperature of 190°C produced samples with superior mechanical properties. Several breathing stages allowed volatiles to escape. After every breathing stage, the pressure was increased in small increments (8.4 MPa). When no more volatiles were produced, moulding continued for another 90 secs. The

final moulding pressure was 25.2 MPa. The mould was subsequently put in a cooled press for approximately 15 mins, followed by demoulding. This moulding cycle produced mouldings 45 mm wide, 130 mm long and approximately 6 mm thick. Three mouldings per compound were made: two for flexural testing and one for impact testing.

#### 3.5 CHARACTERISATION OF CURED MIXTURES AND COMPOUNDS

#### 3.5.1 Comparison of Release Properties

A simple test was carried out in order to check the release properties of a range of internal release agents in J2040L/Polarite 102A mixtures (100 phr filler). Two metal plates were cleaned with acetone and no external release agent was applied. Resin/filler mixtures containing different amounts of internal release agent were placed between the two metal plates and pressed at very low pressures at 190°C. After curing, the samples were removed and cooled in a cold press. The ease with which the metal plates could be separated and how easily the cured resin/filler mixture could be removed was observed. A number on an arbitrary scale between 1 (poor release properties) and 10 (excellent release properties) was awarded reflecting the degree of release.

#### 3.5.2 Measurement of Bulk Density

The effect of compounding temperature on the bulk density of cured resin/filler mixtures was investigated. The cured samples were deflashed, so that square plaques were obtained. These plaques were weighed, and the lengths of their sides measured (average of three measurements). The thickness across the plaque was measured in 9 places, and an average taken. Plaque volume was subsequently calculated and thus an estimate of the plaque bulk density obtained, using the relationship: density = mass/volume (g/cm<sup>3</sup>).

## 3.5.3 Measurement of Flexural Properties

Tests to determine the flexural properties of reinforced plastics are described in the standard test method ASTM D790-M. Two test methods are described: a three-point loading and a four-point loading system. The basic difference between the two test methods is in the location of the maximum axial fibre stresses. The maximum axial fibre stresses occur on a line under the loading nose in three-point loading and over the area between the loading noses in four-point bending. In the case of four-point bending, a much larger area of specimen is effectively under test, which leads to less scatter and more representative results. In this work, four-point bending was used to assess flexural properties. The following configuration was used:

- load/support span ratio = 1/2,
- \* diameter of noses = 10 mm,
- \* test span to specimen depth ratio, L/d = 16 (tolerance of +4 or -2),
- \* rate of crosshead motion = 3 mm/min.
- Figure 3.3 shows the loading diagram.



FIGURE 3.3: Loading diagram for a four-point bending test

The tests were carried out on an Instron TT-DML 10000 kg universal testing machine. The ASTM D790-M standard recommends the following settings for a sample thickness of 6 mm:

- \* specimen width = 10 mm
- \* specimen length = 125 mm
- \* support span = 96 mm
- \* load span = 48 mm
- \* rate of crosshead motion = 2.6 mm/min.

The support span, and as a result the load span, were adjusted for samples with a thickness different from 6 mm, in order to maintain the L/d ratio in the range of 14 to 20.

Flexural strength is given by:

$$FS = \frac{3.P.L}{4.b.d^2}$$

where: FS = flexural strength (MPa),

P = load at the moment of break (N),

L = support span (mm),

b = width of specimen (mm),

d = thickness of specimen (mm).

Flexural modulus for a load span of one half of the support span is given by:

$$FM = \frac{0.17 \text{ L}^3 \text{ m}}{\text{b.d}^3}$$

where:

FM = flexural modulus (GPa),

m = slope of the tangent to the initial straight-line portion of load-deflection curve (N/mm).

For each compound or mixture, six samples were tested at room temperature to obtain an average value. After testing, results of samples which showed large scale imperfections, e.g. large bubbles, where discarded and not taken into account for the calculation of average values. In the case of resin/filler mixtures, the results of on average two of the six samples were not taken into account.

Figures showing flexural and impact properties give one average value per filler loading. For each curve one error bar was included in order to illustrate the amount of scatter that was observed. The error bar gives the range of results for that particular mixture or compound. The full results (the average value plus the range) are given in the Appendix.

#### 3.5.4 Measurement of Impact Strength

Impact testing was carried out on a Rosand instrumented falling weight impact tester, Type 5. The impacter was wedge-shaped. The samples were tested in a three-point loading mode, with a support span of 45 mm. The beam specimen were approximately 6 mm thick, 10 mm wide and had a length greater than 60 mm. The following parameters were set:

drop height	= 207 mm		
impact speed	= 2 m/s		
mass	= 25 kg		
filter	= 1 kHz		
sweep time	= 10 ms		

The peak impact force was measured. For each compound and mixture, six to ten samples were tested. In order to take small differences in thickness into account, a normalisation of the impact strength results was carried out. The peak impact force was divided by the cross-sectional area of the sample. The units of the normalised impact strength are N/mm<sup>2</sup>.

## 3.5.5 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (Cambridge Stereoscan 2 Å) was used to examine the fracture surfaces of mechanically tested cured phenolic dough moulding compounds. Prior to SEM, the fracture surfaces were gold coated in order to increase conductivity and improve the secondary electron yields. A topographic image is formed from the collection of secondary electrons.

# CHAPTER 4 RESULTS

# 4.1 OPTIMUM TWIN SCREW EXTRUDER COMPOUNDING PARA-METERS FOR RESIN/FILLER MIXTURES

The two compounding parameters that were investigated are the barrel temperature and the screw speed. The effect of temperature on the viscosity of unfilled J2040L (high viscosity phenolic resin) is illustrated in Figure 4.1. The effect of adding aminosilane coated china clay (Polarite 102A) on the viscosity of phenolic resin, measured at two different temperatures, i.e. 20 and 50°C, is shown in Figure 4.2.

The effect of compounding temperature on a resin/filler mixture was investigated. A series of mixtures of J2040L and Polarite 420 EW (a calcium carbonate) were prepared using a twin screw compounder at 20 and 50°C. Torque during compounding, expressed as a percentage, was recorded (see Figure 4.3). After curing, the flexural properties were investigated. Figures 4.4 and 4.5 give the flexural strength and modulus respectively of the J2040L/Polarite 420EW mixtures, prepared at the two compounding temperatures. Bulk density of the cured samples was measured and Figure 4.6 gives these results for both compounding temperatures.

The second compounding parameter that has been investigated is screw speed. Over a wide filler loading range, screw speed was varied between 100 and 400 rpm. The effect of screw speed on the viscosity of J2027L/Devolite mixtures is shown in Figure 4.7.

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# 4.2 THE EFFECT OF RESIN TYPE ON THE VISCOSITY OF RESIN/ FILLER MIXTURES

J2040L (high viscosity) and J2027L (low viscosity) phenolic resins were investigated as potential matrices for phenolic moulding compounds. The effect on viscosity of mixing these resins and the deviation of the rule of mixtures is shown in Figure 4.8. The effect of resin viscosity on the resin/filler viscosity is illustrated in Figure 4.9.

#### 4.3 INTERNAL RELEASE AGENTS

The effects of several internal release agents on the release and flexural properties of filled phenolic resin were investigated. Table 4.1 gives the relative release properties and the retention of the flexural properties of the resin/filler/internal release agent mixtures.

# 4.4 THE EFFECTS OF VARIOUS FILLERS ON THE PROPERTIES OF PHENOLIC RESIN

Several china clays, calcium carbonates, dolomite, aluminium trihydrate, wollastonite and combinations of these fillers were investigated as potential fillers for phenolic moulding compounds. Viscosity of the mixtures was measured and after curing, the flexural and impact properties were investigated.

#### 4.4.1 Properties of China Clay Filled Phenolic Resin Systems

The effects of three different types of china clay on the viscosity of phenolic resin can be seen in Figure 4.10.

Figures 4.11, 4.12 and 4.13 illustrate the flexural strength, the impact strength and the flexural modulus respectively of the J2040L/china clay mixtures.

#### 4.4.2 Properties of Calcium Carbonate Filled Systems

Mixtures of calcium carbonates and J2040L were prepared covering a relatively narrow filler loading range. The effects three different types of calcium carbonate have on viscosity are illustrated in Figure 4.14. The flexural and impact strengths of the resin/filler mixtures are given in Figures 4.15 and 4.16. The effects on flexural modulus are shown in Figure 4.17.

#### 4.4.3 Polarite 102A/Dolomite Mixtures

Polarite 102A/dolomite 100/0, 70/30, 50/50, 30/70 and 0/100 mixtures with phenolic resin at different filler loadings were prepared. The effects on viscosity of partially or completely replacing Polarite 102A with dolomite are given in Figure 4.18. The flexural and impact strength results are given in Figures 4.19 and 4.20 respectively. The effects on flexural modulus are illustrated in Figure 4.21. The figures illustrating the mechanical properties only show the Polarite 102A/dolomite 100/0, 50/50 and 0/100 mixtures. The 70/30 and 30/70 mixtures give similar properties to the 50/50 mixture. These mixtures are therefore not included in the aforementioned figures. Full details of the data can be found in the Appendix.

#### 4.4.4 China Clay/Dolomite Mixtures

50/50 mixtures of china clay and dolomite, using three different types of china clay, were prepared. The viscosities of these mixtures are given in Figure 4.22. The flexural and impact strength results are shown in Figures 4.23 and 4.24 respectively. Figure 4.25 illustrates the effects these mixtures have on flexural modulus. Figure 4.56 shows two resin/filler mixtures that were cured using the casting technique.

#### 4.4.5 PoleStar 200R/Aluminium Trihydrate Mixtures

Several filler mixtures of PoleStar 200R and aluminium trihydrate (ATH) have been investigated as filler system for phenolic resin. The effect on viscosity of adding ATH to PoleStar 200R is given in Figure 4.26. The flexural and impact strengths of these mixtures are shown in Figures 4.27 and 4.28. Figure 4.29 illustrates the effect of ATH on the flexural modulus of PoleStar 200R.

#### 4.4.6 Polarite 102A/Wollastonite Mixtures

The effect of wollastonite on the viscosity of J2040L/Polarite 102A mixtures is given in Figure 4.30. Figures 4.31 and 4.32 illustrate the effect of replacing 20 and 40 wt % of Polarite 102A with wollastonite on the flexural and impact strength respectively. The flexural modulus-filler loading relationship of these mixtures is shown in Figure 4.33.

#### 4.5 DOUGH MOULDING COMPOUNDS

#### 4.5.1 Composition Window

A wide range of moulding compound compositions has been prepared using a co-rotating twin screw extruder (see Figure 4.34). Figures 4.35, 4.36, 4.37, 4.38 and 4.39 show uncured compounds, covering wide filler loading and glass fibre content ranges. Figure 4.40 shows an uncured compound rolled into a ball-like dough. After compression moulding the compounds, the flexural and impact properties were measured. Figure 4.57 shows a cured moulding compound containing J2040L, 200 phr Polarite 102A and 25 wt% glass fibre (Owens-Corning R52).

Tables 4.2 and 4.3 give the flexural and impact strengths respectively of the entire composition range that could be prepared with the particular ingredients and processing equipment that were used. The same results are presented in three dimensional graphs in Figures 4.41 and 4.42. Table 4.4 and Figure 4.43 give the flexural modulus results for the range of compounds that were prepared. SEM photomicrographs of cured compounds covering a wide filler loading range are given in Figures 4.44, 4.45, 4.46 and 4.47.

#### 4.5.2 Different Types of Glass Fibres

Three different types of glass fibres were investigated as potential reinforcements in moulding compounds. Tables 4.5, 4.6 and 4.7 illustrate the relative differences in flexural strength for moulding compounds containing different types of glass fibre reinforcements. This data is presented graphically in Figure 4.48. Similarly, the impact strengths for the compounds are given in Tables 4.8, 4.9 and 4.10 or Figure 4.49. The flexural modulus results are given in Tables 4.11, 4.12 and 4.13. SEM photomicrographs comparing the fracture surfaces of cured compounds containing different types of glass fibres are shown in Figures 4.50, 4.51, 4.52 and 4.53.

#### 4.5.3 Extruder Output

The effect of increasing the extruder output on the mechanical properties of moulding compounds was investigated. Table 4.14 shows the effect of extruder output on flexural strength, modulus and impact strength.

#### 4.5.4 Different Types of Fillers

#### 4.5.4.1 Mica

The effects of replacing 50 or 100 wt % of Polarite 102A with mica on mechanical properties have been investigated. Tables 4.15, 4.16 and 4.17 give the flexural strength, modulus and impact strength respectively of these compounds. Figure 4.58 shows a cured compound containing J2040L, 140 phr mica and 20 wt % glass fibres (Owens-Corning R52).

#### 4.5.4.2 Clay/Cellulose Filler Mixtures

Two mixtures of clay and cellulose, i.e. clay/cellulose 70/30 and 30/70, have been investigated as potential fillers for phenolic moulding compounds. Tables 4.18, 4.19 and 4.20 illustrate the effect of the filler mixtures on flexural strength, modulus and impact strength respectively. A SEM photomicrograph of a cured compound containing clay/cellulose 70/30 as filler is shown in Figure 4.55. Figure 4.59 shows a cured sample containing J2040L, 40 phr clay/cellulose 30/70 and 15 wt % glass fibres (Owens-Corning R52).

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TABLE 4.1: Relative release and flexural properties of internal release agents

Legend: 1 = very poor release properties 10 = excellent release properties

Control: J2040L/100 phr Polarite 102A

Type of Additive	Parts per 100 parts of filler	Relative release properties	Flexural strength retention	Flexural modulus retention
			(%)	(%)
Control	0	1	100	100
PAT 660/K	0.5	1	83	108
	1	3	63	88
	2	10	66	58
PAT 664/A	0.5	3	98	102
	1	3	83	95
	2	10	82	90
PAT 659/B	1 2	5 10	72 52	83 63
TR016	1	9	100	96
	2	10	115	95
Mold Wiz	0.5	7	64	78
INT-1854	1	7	62	85
Mold Wiz	0.5	7	61	84
INT-1858	1	8	100	107
#### TABLE 4.2: Composition window: flexural strength of compounds

Resin:J2040LFiller:Polarite 102AGlass Fibre:Owens-Corning R52

Filler load	Glass fibre content (wt %)								
(phr)	10	15	20	25	30	35	40		
40	-	97	109	85	66	-	-		
60	73	51	106	86	95	67	-		
80	-	65	103	83	81	-	-		
100	50	66	66	67	70	68	66		
120	-	60	61	48	67	-	· -		
140	• -	60	45	55	55	-	-		
160	-	55	64	50	41	-	-		
200	-	40	56	43	50	-	-		

#### FLEXURAL STRENGTH (MPa)

TABLE 4.3: Composition window: impact strength of compounds

Resin:J2040LFiller:Polarite 102AGlass Fibre:Owens-Corning R52

#### IMPACT STRENGTH (N/mm<sup>2</sup>)

Filler load		Glass fibre content (wt %)							
(phr)	10	15	<u>20</u>	25	30	35	40		
40	-	7.4	9.6	9.4	7.5	-	-		
60	11.6	-	10.9	5.6	10.1	6.2	-		
80	-	8.4	10.5	8.8	8.5	-	-		
100	4.8	7.2	5.2	6.0	5.6	5.8	5.9		
120	-	6.1	4.0	3.5	6.3	-	-		
140	-	3.9	3.0	3.5	7.2	-	-		
160	-	3.6	3.5	2.4	2.9	-	-		
200	-	3.1	2.8	2.7	-	-	-		

#### TABLE 4.4: Composition window: flexural modulus of compounds

Resin:J2040LFiller:Polarite 102AGlass Fibre:Owens-Corning R52

Filler load	Glass fibre content (wt %)							
(phr)	10	15	20	25	30	35	40	
40	-	23	25	26	28	-	-	
60	22	24	28	29	38	35	-	
80	-	24	32	35	40	-	-	
100	24	28	33	36	41	43	33	
120	-	39	42	43	44	-	-	
140	-	41	43	44	44	-	<b>-</b> .	
160	-	44	45	45	47	-	-	
200	-	46	48	43	46	-	-	

#### FLEXURAL MODULUS (GPa)

TABLE 4.5: Flexural strength of compounds containing Vetrotex P223 glass fibres

Resin: J2040L Filler: Polarite 102A Glass Fibre: Vetrotex P223

#### FLEXURAL STRENGTH (MPa)

Filler load	Glass fibre content (wt %)					
(phr)	10	20	30	40		
60 100 140	66 51 -	106 77 64	99 86 59	63		

## TABLE 4.6: Flexural strength of compounds containing Silenka 087 glass fibres

Resin:J2040LFiller:Polarite 102AGlass Fibre:Silenka 087

#### FLEXURAL STRENGTH (MPa)

Filler load	Glass fibre content (wt %)					
(phr)	10	20	30	40		
60 100 140	76 58 -	123 103 80	111 105 84	- 106 -		

### TABLE 4.7: Flexural strength: comparison between three different types of glass fibre

Resin:	J2040L
Filler:	Polarite 102A
Glass Fibre:	Owens-Corning R52
	Vetrotex P223
	Silenka 087

#### FLEXURAL STRENGTH (MPa)

	Glass fibre content (wt %)						
	20			30			
	Type of glass fibre			Type of glass fibre			
Filler Loading (phr)	R52	P223	087	R52	P223	087	
60 100 140	106 66 45	106 77 64	123 103 80	95 70 55	99 86 59	111 105 84	

## TABLE 4.8: Impact strength of compounds containing Vetrotex P223 glass fibres

Resin:J2040LFiller:Polarite 102AGlass Fibre:Vetrotex P223

### IMPACT STRENGTH (N/mm<sup>2</sup>)

Filler load (phr)	Glass fibre content (wt %)					
	10	20	30	40		
60 100 140	5.0	10.3 5.9 3.4	9.6 6.6 3.3	- 3.6 -		

#### TABLE 4.9: Impact strength of compounds containing Silenka 087 glass fibres

Resin:	J2040L
Filler:	Polarite 102A
Glass Fibre:	Silenka 087

#### IMPACT STRENGTH (N/mm<sup>2</sup>)

Filler load	Glass fibre content (wt %)						
(phr)	10	<sup>′</sup> 20	30	40			
60 100 140	- 5.8 -	13.6 10.4 4.7	12.7 12.2 4.1	- 5.3 -			

TABLE 4.10:Impact strength: comparison between three different types<br/>of glass fibre

Resin: J2040L Filler: Polarite 102A Glass Fibre: Owens-Corning R52 Vetrotex P223 Silenka 087

#### IMPACT STRENGTH (N/mm<sup>2</sup>)

	Glass fibre content (wt %)						
	20			30			
	Тур	e of glass f	ibre	Type of glass fibre			
Filler Loading (phr)	R52	P223	087	R52	P223	087	
60 100 140	10.9 5.2 3.0	10.3 5.9 3.4	13.6 10.4 4.7	10.1 5.6 7.2	9.6 6.6 3.3	12.7 12.2 4.1	

TABLE 4.11: Flexural modulus of compounds containing Vetrotex P223 glass fibres

Resin:J2040LFiller:Polarite 102AGlass Fibre:Vetrotex P223

#### FLEXURAL MODULUS (GPa)

Filler load	Glass fibre content (wt %)					
(phr)	10	20	30	40		
60 100 140	20 27 -	27 43 47	39 44 43	- 43 -		
		1				

TABLE 4.12:Flexural modulus of compounds containing Silenka 087<br/>glass fibres

Resin:J2040LFiller:Polarite 102AGlass Fibre:Silenka 087

#### FLEXURAL MODULUS (GPa)

Filler load	Glass fibre content (wt %)			
(phr)	10	20	30	40
60 100 140	20 22 -	28 39 43	31 40 49	53

- TABLE 4.13: Flexural modulus: comparison between three different types of glass fibre
  - Resin: J2040L Filler: Polarite 102A Glass Fibre: Owens-Corning R52 Vetrotex P223 Silenka 087

#### FLEXURAL MODULUS (GPa)

	Glass fibre content (wt %)					
	20		30			
	Type of glass fibre		Type of glass fibre		ibre	
Filler Loading (phr)	R52	P223	087	R52	P223	087
60 100 140	28 33 43	27 43 47	28 39 43	38 41 44	39 44 43	31 40 49

TABLE 4.14:The effect of extruder output rate on flexural and impact<br/>properties

Resin:	J2040L
Filler:	Polarite 102A
Glass fibre:	Vetrotex P223

Filler loading = 100 phr Glass fibre content = 20 wt %

Extruder output rate	Flexural strength	Impact strength	Flexural modulus
(g/min)	(MPa)	(N/mm²)	(GPa)
100 125 150	77 74 66	5.9 4.4 3.8	43 41 46

TABLE 4.15:

The effect of mica on the flexural strength of compounds

Resin:	J2040L
Glass fibre:	Owens-Corning R52

Glass fibre content: 20 wt %

#### FLEXURAL STRENGTH (MPa)

Filler loading (phr)	Polarite 102A/Mica		
	100/0	50/50	0/100
60	106	48	76
100 140	66 45	55 45	73 78

TABLE 4.16:The effect of mica on the flexural modulus of compounds

Resin:J2040LGlass fibre:Owens-Corning R52Glass fibre content:20 wt %

#### FLEXURAL MODULUS (GPa)

Filler loading	Polarite 102A/Mica		
(phr)	100/0	50/50	0/100
60	28	21	23
100	33	24	27
140	43	26	31

#### TABLE 4.17: The effect of mica on the impact strength of compounds

Resin:J2040LGlass fibre:Owens-Corning R52

Glass fibre content: 20 wt %

#### FLEXURAL MODULUS (GPa)

Filler loading	Polarite 102A/Mica		
(phr)	100/0	50/50	0/100
60	10.9	9.6	9.9
100	5.2	6.5	5.2
140	3.0	6.0	6.7

TABLE 4.18:The effect of clay/cellulose mixtures on the flexural<br/>strength of compounds

Resin:J2040LGlass fibre:Owens-Corning R52

Glass fibre content: 15 wt %

#### FLEXURAL STRENGTH (MPa)

	Clay/Cellulose	
Filler loading (phr)	70/30	30/70
60	-	99
100	80	60
140	38	79

### TABLE 4.19:The effect of clay/cellulose mixtures on the flexural<br/>modulus of compounds

### Resin:J2040LGlass fibre:Owens-Corning R52

Glass fibre content: 15 wt %

#### FLEXURAL MODULUS (GPa)

	Clay/Co	ellulose
Filler loading (phr)	70/30	30/70
60	. •	18
100	14	17
140	11	21

# TABLE 4.20:The effect of clay/cellulose mixtures on the impact strength<br/>of compounds

Resin:J2040LGlass fibre:Owens-Corning R52Glass fibre content:15 wt %

### IMPACT STRENGTH (N/mm<sup>2</sup>)

	Clay/Cellulose		
Filler loading (phr)	70/30	30/70	
60 100 140	9.7 4.7	14.9 11.1 11.0	



TEMPERATURE ( C)

FIGURE 4.1: The effect of temperature on the viscosity of J2040L



FIGURE 4.2: Viscosity of J2040L/Polarite 102A mixtures at 20° and 50°C



FILLER LOADING (PHR)

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FIGURE 4.5:



FIGURE 4.6: Effect of compounding temperature on bulk density





wt % J2027L

.



Effect of type of resin on viscosities of resin/PoleStar 200R mixtures

FIGURE 4.9:



FIGURE 4.10:

Viscosity of china clay systems









FIGURE 4.14:

Viscosity of calcium carbonate systems











FIGURE 4.19: Flexural strength of Polarite 102A/dolomite systems





FIGURE 4.21: Flexural modulus of Polarite 102A/dolomite systems





FIGURE 4.23: Flexural strength of china clay/dolomite 50/50 systems







FILLER LOADING (PHR)

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FIGURE 4.28: Impact strength of PoleStar 200R/ATH systems



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FIGURE 4.31:





FIGURE 4.33:



MATERIALS:

Resin:	J2040L
Filler:	Polarite 102A
Glass fibre:	Owens-Corning R52

FIGURE 4.34: Dough moulding compound composition window



## FIGURE 4.35: Photograph of a compound containing J2040L, 140 phr of Polarite 102A and 20 wt % of Silenka 087



FIGURE 4.36:

Photograph of a compound containing J2040L, 100 phr of Polarite 102A and 20 wt % of Silenka 087



# FIGURE 4.37: Photograph of a compound containing J2040L, 60 phr of Polarite 102A and 20 wt % of Silenka 087



FIGURE 4.38:

Photograph of a compound containing J2040L, 60 phr of Polarite 102A and 30 wt % of Silenka 087



## FIGURE 4.39: Photograph of a compound containing J2040L, 60 phr of Polarite 102A and 10 wt % of Silenka 087



FIGURE 4.40: Photograph of a compound (rolled in ball-shaped dough) containing J2040L, 00 phr of Polarite 102A and 30 wt % of Silenka 087 (same compound as in Figure 4.38)



FIGURE 4.41:

Composition window: flexural strength of compounds



FIGURE 4.42:

Composition window: impact strength of compounds



FIGURE 4.43:

Composition window: flexural modulus of compounds



FIGURE 4.44: SEM photomicrograph of a compound containing J2040L, 200 phr of Polarite 102A and 10 wt % of Owens-Corning R52



FIGURE 4.45: SEM photomicrograph of a compound containing J2040L, 40 phr of Polarite 102A and 20 wt % of Owens-Corning R52



FIGURE 4.46: SEM photomicrograph of a compound containing J2040L, 100 phr of Polarite 102A and 10 wt % of Owens-Corning R52 (detail of Figure 4.47)



FIGURE 4.47: SEM photomicrograph of a compound containing J2040L, 100 phr of Polarite 102A and 10 wt % of Owens-Corning R52



FIGURE 4.48:

Flexural strength: comparison between three different types of glass fibres



FIGURE 4.49:

Impact strength: comparison between three different types of glass fibres



FIGURE 4.50: SEM photomicrograph of a compound containing J2040L, 60 phr of Polarite 102A and 20 wt % of Silenka 087



FIGURE 4.51: SEM photomicrograph of a compound containing J2040L, 60 phr of Polarite 102A and 20 wt % of Silenka 087 (detail of Figure 4.50)



FIGURE 4.52: SEM photomicrograph of a compound containing J2040L, 140 phr of Polarite 102A and 20 wt % of Vetrotex P223



FIGURE 4.53: SEM photomicrograph of a compound containing J2040L, 140 phr of Polarite 102A and 20 wt % of Owens-Corning R52



FIGURE 4.54: SEM photomicrograph of a compound containing J2040L, 60 phr of Polarite 102A/mica 50/50 filler mixture and 20 wt % of Owens Corning R52



FIGURE 4.55: SEM photomicrograph of a compound containing J2040L, 60 phr of clay/cellulose 70/30 filler mixture and 15 wt % of Owens Corning R52



#### FIGURE 4.56: Photograph of cured J2040L/filler mixtures. Sample A contains 166 phr of Polarite 102A/dolomite 50/50 filler mixture Sample B contains 124 phr of dolomite



FIGURE 4.57:

Photograph of a cured PF.DMC containing J2040L, 200 phr of Polarite 102A and 25 wt % of Owens-Corning R52



FIGURE 4.58: Photograph of a cured PF.DMC containing J2040L, 140 phr of mica and 20 wt % of Owens-Corning R52



FIGURE 4.59:

Photograph of a cured PF.DMC containing J2040L, 40 phr of clay/cellulose 30/70 filler mixture and 15 wt % of Owens-Corning R52

## CHAPTER 5 DISCUSSION

## 5.1 OPTIMUM TWIN SCREW EXTRUDER COMPOUNDING PARA-METERS FOR RESIN/FILLER MIXTURES

The optimum compounding characteristics for a co-rotating twin screw compounder were investigated. Mixtures of phenolic resin and several particulate fillers were prepared using two compounding temperatures and a range of screw speeds.

#### 5.1.1 Compounding Temperature

The effect of temperature on the viscosity of J2040L is shown in Figure 4.1. Increasing the temperature from 20 to 50°C reduces the viscosity by a factor of ten.

Figure 4.2 illustrates the effect of temperature on the viscosity of Polarite 102A filled J2040L phenolic resin. The mixtures were prepared using a twin screw extruder at 50°C. After storing the samples at sub-zero temperatures in a freezer, viscosity was measured at two different temperatures (20 and 50°C). As for the unfilled samples, a drastic drop in viscosity is observed when the temperature is increased from 20 to 50°C.

Mixtures of J2040L and Polarite 420EW were prepared using a twin screw compounder at 20 and 50°C. Torque during compounding, expressed as a percentage, was recorded. Figure 4.3 shows the torque-filler loading relationship for the two compounding temperatures. At the higher temperature (i.e. 50°C), the decrease in viscosity of phenolic resin lowers the overall viscosity of the mixture. The twin screw compounder therefore, uses less power (lower torque) in order to mix the components. The lower the mixing temperature, the higher the compound viscosity and consequently the higher

the torque. Measuring torque at mixing temperature, i.e. 50°C does not indicate the viscosity level at 20°C. When cooled down, the mixture compounded at 50°C stiffened up to such an extent that viscosity could not be measured, i.e. the samples could not be completely squeezed out between the cone and plate. Samples with similar filler loadings but compounded at 20°C showed lower viscosities at room temperature, i.e. indicated by being able to take measurements on the cone and plate viscometer. When filler and resin are compounded at 50°C, the low viscosity of the resin enhances wetting out of the filler, a relative low viscosity is observed, provided the compound is kept at that temperature. However, once the compound cools down, the resin viscosity increases and, as a result of good wetting out of the filler, a higher compound viscosity is observed than in the case where the filler wetting out is not that good (i.e. at a compounding temperature of 20°C). Wetting is understood to be the spreading and/or absorption of resin on or into the filler surface. Due to the short residence time (depending on screw speed: 20-45 secs) and narrow residence time distribution in the twin screw compounder, the high viscosity at room temperature of samples compounded at 50°C is not likely to be the result of premature crosslinking of phenolic resin.

The improved wetting out of samples compounded at 50°C is further illustrated in the flexural strength and modulus results (see Figures 4.4 and 4.5) where mixtures originally compounded at 50°C, were found to have a higher flexural strength and modulus than mixtures prepared at 20°C.

The effect of compounding temperature on the density of cured samples has been investigated. Graphs of bulk density versus filler loading for the two different compounding temperatures are shown in Figure 4.6. At a compounding temperature of 50°C, the improved wetting out of the filler surface results in less intra and interagglomerate voids in the cured compound. This is reflected in the higher bulk density values for samples compounded at 50°C. Compounding at a lower temperature results in higher levels of shear in the extruder. This will

result in a reduction of the average particle size and consequently in a reduced packing fraction and hence a lower bulk density [Wypych].

#### 5.1.2 Screw Speed

The effect of screw speed of a twin screw compounder on viscosity is shown in Figure 4.7. Mixtures of low viscosity phenolic resin (J2027L) and china clay (Devolite) were prepared using different screw speeds. There is no clear trend indicating the effect of screw speed on viscosity. In particular, at low filler loadings, there is no significant difference in viscosity between mixtures prepared at 100 or 400 rpm. This indicates that similar degrees of dispersion and filler wetting out are achieved over the screw speed range that has been investigated.

Figure 4.7 also shows the maximum conveying capacity at each screw speed for this particular filler (Devolite). The twin screw compounder has a small conveying capacity of material at low screw speeds, i.e. only small amounts of material can be displaced. For a fixed resin feed this equipment limitation can limit the range of compositions which can be produced. For instance, it was found at a screw speed of 100 rpm, Devolite can be incorporated only up to 88 phr before over-saturation in the barrel occurs, resulting in blocking of the feed hopper. At high screw speeds, it is more likely that the extrudability of the compound will limit the filler loading. When a twin screw extruder is starve-fed, the two primary variables are feed rate and screw speed for a particular screw configuration.

### 5.2 THE EFFECT OF RESIN TYPE ON THE VISCOSITY OF RESIN/FILLER MIXTURES

J2040L (high viscosity) and J2027L (low viscosity) phenolic resins were investigated as potential matrices for phenolic moulding compounds. The viscosity of these resins is controlled by the degree of condensation (i.e.

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particular values of average molecular weight and molecular weight distribution) and the water content of the resin (see section 2.1.1.3). J2027L has a lower degree of condensation and contains more water than J2040L. The effect on viscosity of mixing these resins is illustrated in Figure 4.8. The theoretical viscosity according to the law of mixtures is also given. Adding small amounts of J2027L to J2040L resin reduces the overall viscosity to a greater extent than the law of mixtures would suggest. This is in agreement with Knop and Pilato who found that small amounts of water reduce viscosity substantially.

Mixtures of PoleStar 200R with J2027L and J2040L were prepared. The effect of filler loading on viscosity was measured and is shown in Figure 4.9. The difference in viscosity between mixtures containing different resins is substantial (nearly a factor of ten).

Although it is possible to heat cure the low viscosity resin (J2027L), it was originally designed as an acid cure system. The high viscosity resin (J2040L) on the other hand, is designed as a heat cure system. The advantage of using a low viscosity resin is that good wetting out of filler and glass fibre can be achieved. The disadvantages however, are a longer cure time and a higher degree of porosity in the cured sample. The increased level of porosity is due to the lower original molecular weight and the higher water content in the resin (more volatiles are driven off during cure). The high viscosity resin has a shorter cure time and contains less voids. However, the disadvantage is the inferior glass fibre and filler wet out. This negative point can be circumvented by compounding the ingredients at a higher temperature which decreases the viscosity, resulting in improved degree of wetting out. After cooling down, the viscosity increases again and the advantages of using a high viscosity resin still hold. The effect of temperature on the viscosity of J2040L is illustrated in Figure 4.2. High viscosity resin at 50°C has approximately the same viscosity as the low viscosity resin at 20°C.

As a result of these trials, it was decided that further work would involve the use of high viscosity resin J2040L.

#### 5.3 INTERNAL RELEASE AGENTS

Mixtures of J2040L and 100 phr Polarite 102A with a variety of internal release agents were prepared (see Table 3.5) and their flexural and release properties tested (see Table 4.1).

Internal release agents containing fatty acid derivatives (PAT 659/B), a water dispersion of waxes (PAT 664/A) and organic acid derivatives (PAT 660/K) were investigated. Two internal release agents based on polymeric resins (further details regarding the exact compositions were not available) were also investigated, i.e. Mold Wiz INT-1854 and INT-1858. TR016 contains calcium soap with a fatty acids amine. TR016 is a fine powder, while all the others are low viscosity liquids. These additives are soluble in the phenolic compound at room temperature. At the curing temperature, i.e. 190°C, the internal release agent becomes insoluble from the polymeric mass, and phase separates tends to migrate to the mould surface where it aids subsequent mould release.

At a loading of 2 parts of mould release to 100 parts of filler, all types of internal release agent showed excellent release properties. The difficulties associated with the accurate metering of very small amounts of a low viscosity liquid into a relatively high viscosity resin/filler mixture mean that it is more practical to use an internal release agent in the form of a powder. The powder is readily mixed with filler prior to compounding. Addition of TR016 to Polarite 102A resulted in a higher flexural strength, compared to a reduction as is seen for all but one of the liquid internal release agents.

As a result of these tests, it was concluded that in further work 2 parts of TR016 to 100 parts of filler would be added to the compound. Compounds with low filler loading showed substantial shrinkage, which made mould release relatively easy. Compounds with higher filler loadings shrink less and therefore create more difficulties at demoulding. Depending on the filler loading, different amounts of internal release agent were added to the moulding compound (the percentage of mould release to filler remained unchanged).

## 5.4 THE EFFECTS OF VARIOUS FILLERS ON THE PROPERTIES OF PHENOLIC RESIN

It was felt necessary to study the interaction of resin with different particulate fillers without the influence of glass fibres, as these would induce further variation due to orientation and variable glass fibre length. The effects of several china clays, calcium carbonates, dolomite, aluminium trihydrate, wollastonite and combinations of these fillers on the viscosity, flexural properties and impact strength of phenolic resin were investigated. Generally, mechanical properties of filled materials depend on polymer-polymer interaction, the interaction between polymer matrix and filler particles and the interaction between filler particles. In order to reinforce a polymer matrix, a filler has to have a much higher modulus than the matrix, the interfacial bonding between filler and matrix must be stronger than the matrix, the filler size should not exceed 25 µm and finally the amount of filler added must allow for perfect wetting and interaction. If this is not the case, filler decreases tensile strength and modulus, or such a decrease is observed above a certain filler concentration, because filler introduces defects in the matrix structure, rather than reinforcing it. When filler and matrix do not give rise to a strong interfacial bond, voids are easily formed at the filler poles (areas on either side of the filler in the direction of the applied deformation). The tensile strength is reduced to a greater extent when filler hardness is high, because the matrix around the particles is additionally affected by the stress perpendicular to the direction of the sample extension [Wypych].

The effect of filler on viscosity has been studied extensively and several formulas have been suggested. However, parameters such as surface chemistry of fillers, irregular particle shapes and particle size distributions have not yet been accounted for. One of the earlier formulas, suggested by Einstein, describing the viscosity of dispersions is given in Formula 5.1,

$$\eta = \eta_{o} (1 + 2.5 \phi)$$
 (5.1)

where  $\eta$  = viscosity of filled system,

 $\eta_o$  = viscosity of dispersing phase and

 $\phi$  = volume fraction of filler.

The non-linear increase of viscosity, at higher additions of filler, is not accounted for by Einstein's equation. Further equations were developed, based on Formula (5.1), by Guth, Simha and Gold and Lee. These equations are correct for a limited number of systems, narrow temperature range, and low additions of filler to Newtonian liquids. The Mooney equation (Formula (5.2)) characterises the relationship between viscosity of a filled system, filler content and its packing volume,

$$\eta = \eta_{o} \exp\left[\frac{k\phi}{1 - \phi/P_{f}}\right]$$
(5.2)

where k = Einstein constant

P,

volume packing, i.e. the fraction of unitary space occupied
by filler particles when close-packed in dense random
packing.

When the amount of filler increases, the increase in solid content results in an increased viscosity. When particle size increases, specific surface area decreases and packing fraction increases, resulting in a higher viscosity. Surface character affects viscosity to a greater extent than the particle size of the filler. Filler concentration has a larger effect on viscosity than filler structure [Wypych].

#### 5.4.1 Properties of China Clay Filled Phenolic Resin Systems

The effects of various china clays on properties such as viscosity, flexural and impact strength and flexural modulus can be quite diverse. Three different china clays have been investigated as potential fillers for phenolic resin: PoleStar 200R, Polarite 102A and Devolite. More information regarding these china clays can be found in Chapter 3.1.2.1.

#### 5.4.1.1 Viscosity

The effects of these fillers on the viscosity of phenolic resin can be seen in Figure 4.10. For each of the fillers, the results show that viscosity increases with filler content. Devolite has a relatively large average particle size and low surface area (7  $m^2/g$ ), which results in Devolite filled systems giving rise to the lowest viscosity of the three systems.

PoleStar 200R has an identical surface chemistry but a larger surface area (8.5  $m^2/g$ ) than Devolite and therefore leads to a higher viscosity on a weight to weight basis. The fact that Polarite 102A filled systems have the highest viscosities is attributed to the aminosilane coating of the filler which has an affinity for phenolic resin. The filler coating also improves dispersion which results in a greater filler surface area to volume ratio. This gives rise to the higher viscosity of Polarite 102A filled systems.

#### 5.4.1.2 Mechanical properties

The effects of the three china clays on flexural strength, modulus and impact strength are illustrated in Figures 4.11, 4.12 and 4.13. Adding a particulate filler to a brittle matrix usually decreases the flexural and impact strengths and increases the flexural modulus.

At a low filler loading, e.g. 60 phr filler, there is very little difference in flexural and impact strength between the three types of china clay. Particle size and filler surface do not have an effect on these properties. Phenolic resin has a relatively high coefficient of thermal expansion (40-60  $10^{-6}$ /°C) and low elongation at break (1-1.5%). Resin/filler mixtures with only small amounts of filler have a high degree of shrinkage. Combined with low elongation at break, this may result in the formation of microcracks in the resin. Both Devolite and PoleStar 200R are untreated fillers and therefore have a very weak interface with phenolic resin. Polarite 102A is an aminosilane coated filler and has a much stronger resin/filler interface than the untreated fillers. The high levels of shrinkage will lead to internal stresses, especially near the resin/filler interface.

As a result, the interfaces are severely stressed and both strong and weak interfaces are (further) weakened. Interfacial stresses, which further develop when the composite is subject to mechanical stress, can result either in adhesive failure at the interface or in cohesive failure of the matrix polymer adjacent to the interfaces [Solomon and Hawthorne].

Filler particles can act as stress concentrators. A strong interface is imperative for the flexural strength of a composite. Impact strength, on the other hand, depends to a lesser extent on the strength of the interface. As a rule of thumb, optimum impact strength is obtained when interfacial strength is approximately 20% of the matrix shear strength. Therefore, interfacial stresses due to shrinkage affect impact strength to a lesser extent than flexural strength. At 60 phr, flexural strength decreases twice as much as impact strength does.

As the filler loading increases, there will be less shrinkage. Consequently, the interfacial stresses will be smaller and the composite properties will depend more on the type and size of filler and the strength of the resin/filler interface. Therefore, differences in mechanical behaviour between treated and untreated fillers are observed as a result of the increased importance of the filler type.

The aminosilane treated filler, Polarite 102A, markedly increases the flexural and impact strengths from 60-80 phr filler onwards. The reasons for this increase are twofold. First during cure, the aminosilane coating on the filler chemically reacts with phenolic resin, creating a strong interface. Second, in general, filler coatings aid the separation of filler particles and the stabilisation of the dispersion [Plueddemann]. The flexural and impact strengths of the systems containing untreated fillers remain low due to the weak resin/filler interface. The two types of untreated filler, PoleStar 200R and Devolite, have different average particle sizes. Both fillers are chemically and structurally similar. At the same filler loading (by weight), the interfacial area between resin and filler will be greater for the filler with the smallest average particle size, i.e. PoleStar 200R, as a results of its larger filler surface area to volume ratio. As mentioned above, untreated filler acts as a stress concentrator (areas of the interface which are not in contact may act as cracks under an applied stress) and therefore, the larger the interfacial area the weaker the composite. The impact strength of PoleStar 200R filled systems is consistently lower than that of Devolite filled systems. So, in the case of untreated fillers it is - up to a point - better to have fewer large particles instead of many smaller ones. Others have studied the effect of the glass bead diameter on the Charpy notch toughness of filled polyethylene. They found that the notch toughness increases with increasing glass bead diameter [Svehlova and Poloucek].

The difference in flexural strength between PoleStar 200R and Devolite containing resin/filler mixtures is not great and statistically insignificant. Inter-particle distance has an influence on the level of filler loading that will

result in a change in mechanical properties. Polarite 102A and PoleStar 200R have the same average particle size and particle size distribution. Impact strength changes markedly at a critical filler content of 60 phr. As Devolite is a larger filler, the same interparticle distance is achieved at a higher filler loading (per weight). Devolite filled systems show a decrease in impact properties at a higher critical filler content of about 80 phr.

Flexural modulus increases with filler loading (see Figure 4.13). At low filler loadings, filler has little or no effect on composite modulus due to high levels of shrinkage. Flexural modulus remains roughly at the level of unfilled phenolic resin, i.e. 6.6 GPa. At higher filler loadings, the aminosilane coated filler affects flexural modulus to a greater extent than do the untreated fillers, as a result of the more efficient transfer of stresses across the interface. PoleStar 200R filled systems, which have a larger interfacial area, have a higher modulus than Devolite composites. Nakamura and co-workers found that in epoxy resin filled with angular-shaped silica, the flexural modulus slightly increases while the tensile modulus slightly decreases as the particle size increases. They also found that increasing the specific area of filler particles, i.e. reducing the average particle size, increases the tensile and flexural strength of the particulate filled composite. The findings of Nakamura and co-workers lead to quite different conclusions as the ones obtained in this work [Nakamura *et al*].

Wypych however, suggests the simultaneous effect of two parameters: particle size and surface activity. Modulus increases when particle size decreases, and concentration of active groups on the surface increases. A study of polyester resin/dolomite mixtures carried out by Norwegian Talc also indicates that a decrease in particle size results in an increased flexural modulus [Norwegian Talc]. The difference is that Nakamura and co-workers studied systems that involve fillers acting as a reinforcement. However, uncoated china clay fillers, are not reinforcing and particle size affects strength and modulus results differently.

#### 5.4.2 Properties of Calcium Carbonate Filled Systems

Four types of calcium carbonate have been investigated as potential fillers for phenolic moulding compounds: Britomya V, Albarex, Omya BL and Polarite 420 EW, as detailed in Chapter 3.

#### 5.4.2.1 Viscosity

Resin/filler mixtures containing Britomya V have higher viscosities than Albarex filled systems (see Figure 4.14). As a result of the fatty acid surface coating, Albarex has a lower DOP (dioctylphthalate) absorption and thus a lower viscosity than Britomya V mixtures. Britomya V has a smaller average particle size than Albarex: this will also result in a higher viscosity for Britomya V filled systems.

Omya BL mixtures cover a higher filler loading range than Albarex and Britomya V filled systems and it is therefore difficult to make direct comparisons or to extrapolate between these fillers. However, carefully extrapolating the Albarex data to higher filler loadings indicates that Omya BL mixtures would have a higher viscosity than Albarex filled systems. Although both fillers have the same average particle size, i.e. 5  $\mu$ m, Albarex is a fatty acid coated filler with lower absorption characteristics and therefore its mixtures have lower viscosities than Omya BL filled systems.

The effects and problems associated with Polarite 420 EW mixtures have been discussed in Section 5.1.1.

#### 5.4.2.2 Mechanical properties

The effects of calcium carbonates on flexural and impact strength are shown in Figures 4.15 and 4.16. Polarite 420 EW mixtures have inferior strength properties compared to other calcium carbonates. The polymeric coating - vinyl or acrylic based - designed specifically for polyester moulding compounds and which would normally react with the unsaturated polyester resin's curing agent,

e.g. styrene, does not interact with the phenolic matrix. The resin/filler interface, therefore, is weak giving poor flexural and impact strength properties. The effect of Polarite 420 EW on flexural modulus is illustrated in Figure 4.17. The flexural modulus value at a Polarite 420 EW filler loading of 250 phr is not in line with the flexural modulus values of the resin/filler mixtures at higher filler loadings. The reason for this anomaly is unclear.

Like the viscosity data, it is difficult to extrapolate results in order to compare different fillers. The filler loadings that were used for different filler mixtures are the result of practical considerations during the compounding stage. At the compounding temperature, i.e. 50°C, the absorption characteristics of the filler and consequently the viscosity of the extruded mixture determined what filler loading range could be incorporated in the phenolic resin. Even taking the difficulty of extrapolating into account, it can be seen from Figure 4.17 that Polarite 420EW filled systems have, compared to other calcium carbonate filled systems, a relatively low flexural modulus. This is the result of the poor resin/filler interface.

Although better than Polarite 420 EW mixtures, the flexural and impact strengths of Albarex, Britomya V and Omya BL filled systems are quite poor. The effect of these three fillers is very similar. Omya BL mixtures obtain similar strength properties to Britomya V and Albarex filled systems, but at a filler loading of approximately 100 phr higher.

Impact and flexural strength of Albarex and Britomya V are very similar (except for the Britomya V mixture at 180 phr). It seems that the fatty acid coating on Albarex does not deteriorate the resin/filler interface any further. Britomya V filled systems also have a weak interface. Both types of filler result in weak interfaces. This could be the reason why very little difference in strength is observed between the two fillers. However, there is a pronounced difference
in flexural modulus between Albarex and Britomya V filled systems. The reason why Albarex mixtures have a lower flexural modulus may be as follows: the fatty acid coating which does not improve the weak interface of an untreated filler, may act as a boundary layer between the matrix and the filler. This "plasticising" layer may therefore reduce the effect filler has on flexural modulus.

Britomya V mixtures, after careful extrapolation, have a higher modulus than Omya BL. This is in line with the flexural modulus results of china clay filled systems. The smaller the filler, the greater the interfacial area and its subsequent effect on modulus.

#### 5.4.3 Polarite 102A/Dolomite Mixtures

Polarite 102A/dolomite 100/0, 70/30, 50/50, 30/70 and 0/100 mixtures with phenolic resin at different filler loadings were prepared. Replacing some of the relatively expensive Polarite 102A with cheap dolomite has considerable commercial benefits. This is of great importance in the moulding compound industry which is mainly involved in high volume, low cost products. The effects on viscosity, flexural and impact properties were investigated.

#### 5.4.3.1 Viscosity

Figure 4.18 shows the effects different Polarite 102A/dolomite mixtures have on viscosity. Polarite 102A has a smaller average particle size than Microdol H400 (dolomite). This, in combination with the aminosilane coating explains the higher viscosity of Polarite 102A mixtures compared to dolomite filled systems. Dolomite also has a small surface area, i.e. 0.9 m<sup>2</sup>/g, compared to Polarite 102A (8.5 m<sup>2</sup>/g). Mixing large and small particles has an effect on packing characteristics. Work done by several workers shows optimum packing efficiency can be achieved by mixing 73 v% large with 27 v% small particles [German, Cumberland and Crawford]. The absolute size of these large or small particles is not important; only the fact that two types of particles with different sizes are available is relevant. This results in the highest packing density for these particular particles. For a particular filler loading (per weight), good filler packing leaves a greater proportion of volume of material available for resin and therefore results in a resin/filler mixture of lower viscosity.

The results shown in Figure 4.18 agree with the theory. Blends of Polarite 102A/dolomite 30/70, i.e. 30 wt% small and 70 wt% large particles, have the lowest viscosity. The difference in density between the two fillers is quite small (Polarite 102A: 2.6 g/cm<sup>3</sup> and dolomite: 2.85 gr/cm<sup>3</sup>). Taking this difference into account translates a 30/70 weight ratio into a 31.9/68.1 volume ratio. The viscosity levels of the other mixtures lie between the values of the 30/70 and 100/0 mixtures.

#### 5.4.3.2 Mechanical properties

Both the flexural and impact strength results (Figures 4.19 and 4.20) show similar trends for the different Polarite 102A/ dolomite mixtures.

At low filler loadings, i.e. below 50 to 60 phr filler, there is little difference in mechanical properties between the different filler mixtures. As with china clay filled systems, the large amount of shrinkage causes the matrix and/or the resin/filler interface to fail under stress, regardless of filler type. The smaller of the two fillers, i.e. Polarite 102A, has a greater interfacial area than dolomite. This means that there is a greater area over which stress concentrations can develop. Therefore, the flexural strength of formulations with increasing loadings of Polarite 102A decreases at relatively lower filler contents than does that of the dolomite filled systems. No such reduction in impact strength is observed for the Polarite 102A mixtures. This can be attributed to the relative importance of the resin/filler interface to flexural and impact strength (this has been described for china clay filled systems in Section 5.4.1.2).

With increasing filler loading, the amount of shrinkage decreases and the effect of filler type on mechanical properties becomes more important. Dolomite consists of both magnesium and calcium carbonates. When dissolved in water, small amounts of impurities such as calcium hydroxide and particularly magnesium hydroxide result in an increased degree of alkalinity of the resin/filler slurry. Phenolic resins suffer a deterioration of their mechanical properties when exposed to an alkaline environment. Impurities in dolomite, dissolving in an aqueous medium like resol resin and thus increasing the pH, could explain the sharp reduction in strength of resin/dolomite mixtures. The decrease in flexural and impact strength occurred at the same filler loading level, i.e. 70 phr of filler. However, further work is necessary in order to confirm this hypothesis.

50/50 mixtures of Polarite 102A and dolomite show flexural and impact strengths between the two fillers. 70/30 and 30/70 mixtures have very similar strength properties and this data is not included in the graph. The results of the 70/30 and 30/70 mixtures can be found in the Appendix. At high filler loadings, the flexural strength of Polarite 102A/dolomite mixtures lies between the strength of pure Polarite 102A and dolomite filled systems. The flexural strength of Polarite 102A filled systems will decrease at higher filler loadings, as the amount of resin available to wet out the filler surface is being reduced.

The effects of the filler mixtures on flexural modulus are illustrated in Figure 4.21. Polarite 102A filled systems consistently exhibit the highest flexural modulus. The small average particle size and the presence of an aminosilane coating result in good interfacial properties over a relatively large surface area. Dolomite, a filler with a larger average particle size, shows an increase in flexural modulus at higher filler loadings. From a filler loading of 120 phr onwards, flexural modulus increases sharply. However, it might be argued that dolomite is very plate-like and may therefore offer greater resistance to flexure,

i.e. by having a high flexural modulus, if a significant number of particles is present in the plane of stress.

Mixtures of the two fillers (Polarite 102A and dolomite) have flexural moduli which reflect the moduli of both individual fillers. For example, the Polarite 102A/dolomite 50/50 mixture shows two separate increases in modulus : one reflecting the Polarite 102A filler content and a second increase coinciding with the presence of dolomite. The data that illustrates this is not included in the graph as only a relatiely small filler loading range is shown. Only the 30/70 mixture has flexural modulus values outside the Polarite 102A and dolomite limits (see Appendix).

#### 5.4.4 China clay/dolomite mixtures

50/50 mixtures of china clay and dolomite, using three different types of china clay, were prepared. Their effects on viscosity, flexural properties and impact strength were investigated. The three types of china clay and dolomite involved are the same ones that have been described earlier, i.e. Polarite 102A, PoleStar 200R, Devolite and Microdol H400.

#### 5.4.4.1 Viscosity

The viscosities of 50/50 mixtures of china clay with dolomite are shown in Figure 4.22. The same trends are observed as for the china clay filled systems where no dolomite was added.

The effects the three different china clays have on viscosity (see Section 5.4.1.1) are maintained when half of the china clay is replaced by dolomite. The differences in viscosity of the three china clays however, are smaller as dolomite is introduced. Adding dolomite to the china clay filled systems reduces the viscosity by nearly a factor of ten.

#### 5.4.4.2 Mechanical properties

It can be seen from Figure 4.23 that Polarite 102A/dolomite filled systems have superior flexural strength compared to the other china clay/dolomite mixtures; incorporating 100 phr of this filler system reduces flexural strength by less than 20%. Both other filler systems (PoleStar 200R/dolomite and Devolite/ dolomite) have their flexural strength, at the same filler loading, reduced by approximately 70%. With the exception of the Devolite/dolomite mixture at 76 phr, the difference in flexural strength between PoleStar 200R and Devolite containing mixtures is minimal and within statistical error margin. The reason why the Devolite/dolomite mixture at 76 phr has a much higher flexural strength is unclear.

The effects of these filler mixtures on flexural modulus (see Figure 4.25) are confusing. Polarite 102A/dolomite filled systems result in the highest modulus values. This confirms the flexural modulus results from the china clay filled systems, where the highest moduli were observed for Polarite 102A mixtures. The large scatter in the Devolite/dolomite results and the drop in modulus of PoleStar 200R/dolomite mixtures were not anticipated.

The effects of these filler mixtures on impact strength are shown in Figure 4.24. In addition to the data for the filler mixtures, the impact data for dolomite are also given. Polarite 102A/dolomite 50/50 mixtures have impact properties which are intermediate to the two individual fillers (see Figure 4.20). At relatively high filler loadings, i.e. above 75 phr onwards, failure in dolomite containing filler systems may be precipitated by the higher alkalinity of the resin/fillers mixtures. In the case of Polarite 102A/dolomite mixtures, good interfacial properties between Polarite 102A and phenolic resin mean that the reduction in strength is limited. Impact properties of PoleStar 200R and Devolite/dolomite mixtures are very similar to those of dolomite filled systems. Once the matrix has been weakened as a result of the alkaline environment, failure proceeds with the presence of untreated filler particles as stress concentrators (see Section 5.4.1.2). The distance between the china clay particles and/or the amount of interfacial area determines the rate at which crack propagation occurs. Again, as for china clay filled samples (see Figure 4.12), this is the direct result of the particle size of the filler. PoleStar 200R has a smaller average particle size than Devolite. Therefore, at a given filler loading, it has a larger interfacial area and smaller inter-particle distance than that of Devolite. This translates into a lower impact strength of PoleStar 200R based systems.

Figure 4.56 shows two cured resin/filler plaques. Sample A contains 166 phr of Polarite 102A/dolomite 50/50 filler mixture. The difficulties with casting this material (as described in Chapter 3.4.1) are illustrated by the numerous pores. Sample B contains 124 phr dolomite and has a superior surface finish.

#### 5.4.5 PoleStar 200R/Alumina Trihydrate Mixtures

Several mixtures of PoleStar 200R (china clay) and Trihyde ON4608 (alumina trihydrate (ATH)) have been investigated. These filler systems were studied in order to determine how the incorporation of ATH affects viscosity, flexural properties and impact strength. It was not the intention to study different ratios of PoleStar 200R/ATH covering a wide filler loading range. Two data points for the 50/50 mixture and one data point for the 70/30 and 30/70 mixtures were determined.

#### 5.4.5.1 Viscosity

The effects of PoleStar 200R/ATH 100/0, 70/30, 50/50 and 30/70 mixtures on viscosity are shown in Figure 4.26. Viscosity of the PoleStar 200R/ATH 50/50 mixture at a filler loading of 242 phr was too high to be measured using a cone and plate viscometer. The mixtures that were prepared cover the same viscosity range, i.e. between 2000 and 5000 Pa.s. Replacing PoleStar 200R with ATH required larger amounts of the filler mixture in order to maintain a similar viscosity, thus allowing higher filler loadings to be incorporated. ATH has

a larger average particle size than PoleStar 200R. As mentioned above (Section 5.2.3.1), mixtures of 27 v% small and 73 v% large particles result in optimum packing characteristics and subsequently the lowest viscosity. This can be seen in Figure 4.26 where the PoleStar 200R/ATH 30/70 filler system has a similar viscosity to PoleStar 200R, but at a filler loading of 194 phr cf 128 phr. Adding ATH to PoleStar 200R reduces the viscosity.

#### 5.4.5.2 Mechanical properties

Figures 4.27 and 4.28 illustrate the flexural and impact strength changes over a wide range of filler loading. Both flexural and impact strength are not altered significantly by replacing china clay with different amounts of ATH. Flexural modulus (see Figure 4.29) is reduced by approximately 10-15% when ATH is added. This could be because of the reduced total interfacial area when ATH is introduced into the filler system.

#### 5.4.6 Polarite 102A/Wollastonite Mixtures

100/0, 80/20 and 60/40 mixtures of Polarite 102A and wollastonite (Vansil EW-20) were prepared and tested for viscosity, flexural properties and impact strength.

#### 5.4.6.1 Viscosity

It can be seen from Figure 4.30 that replacing 40 wt% of china clay with wollastonite approximately halves the viscosity. The viscosity of the 80/20 mixture at 178 phr was too high to be measured using a cone and plate viscometer.

Higher filler loadings of wollastonite containing filler mixtures are required in order to maintain similar levels of viscosity as when china clay is the only filler present. Wollastonite is an acicular filler with an aspect ratio of 5:1 and has a larger average particle size (equivalent spherical diameter) and a smaller

surface area than Polarite 102A. This explains the lower levels of viscosity of wollastonite containing mixtures.

#### 5.4.6.2 Mechanical properties

Due to the different filler loading ranges that have been covered for the china clay filled systems on the one hand and the wollastonite containing mixtures on the other hand, there are some difficulties when comparing the mechanical properties of the different filler systems. Flexural and impact strength results are given in Figures 4.31 and 4.32. The flexural modulus of wollastonite/china clay systems is illustrated in Figure 4.33. These graphs show that there is very little difference in properties between the 80/20 and 60/40 filled systems. Although one has to be cautious when extrapolating data, it can be seen that wollastonite does not have a very large influence on flexural modulus.

#### 5.5 DOUGH MOULDING COMPOUNDS

In this section, properties of moulding compounds containing phenolic resin (J2040L), filler(s) and glass fibres are discussed. The effects of filler loading, glass fibre content, types of filler and glass fibre, and extruder output on the mechanical properties of moulding compounds were investigated.

#### 5.5.1 Composition Window

The range of moulding compound compositions, i.e. the composition window, that can be produced on a MP2030 co-rotating twin screw extruder is shown in Figure 4.34. The composition window shown in the ternary diagram is valid only when J2040L, Polarite 102A and Owens-Corning R52 glass fibre are used. The use of different ingredients may result in a change of the composition window. For instance, a similar filler with a smaller average particle size would, due to its larger surface area, result in a higher viscosity compound. This would reduce the maximum amount of filler that could be incorporated into the moulding compound. The method that was used to introduce glass fibre into the

extruder (see Chapter 3.2.2), limits, for a certain glass fibre content, the maximum amount of filler that can be incorporated. Low glass fibre contents can be achieved by lowering the extruder screw speed. However, this reduces the conveying capacity of the extruder (less material is displaced per unit of time). Therefore, at a certain screw speed, feed rate is limited by the conveying capacity of the extruder. In the case of compounds containing 10 wt % glass fibre, 140 phr of filler proved to exceed the conveying capacity. This resulted in blocking of the feed hopper. This problem could be avoided in the future by using glass fibres having a linear density of 600 rather than 2400 tex. Changing the overall output rate of the process would also increase the size of the current composition window.

Another limitation is experienced at high glass fibre loadings, e.g. 40 wt %. The viscosity of the resin/filler mixture needs to be sufficient in order to "carry" the glass fibres through the diehead. When the viscosity is too low, glass fibres block the diehead and the resin/filler slurry emerges from the glass fibre feed port upstream in the extruder barrel. For instance at 40 wt % glass fibres, 60 phr of Polarite 102A filler increased the viscosity insufficiently, and as a result, the diehead became congested. At intermediate glass fibre loadings, i.e. between 10 and 40 wt %, similar difficulties occurred. However, the problems were associated with either very high or very low filler loadings and consequently of limited practical interest.

For any moulding compound, both the average glass fibre length and the degree of wetting out (of both glass fibres and fillers) have an important effect on the ultimate mechanical properties. During the processing of fibre reinforced polymers using co-rotating twin screw extruders, an operating window needs to be established in which the correct balance is struck between fibre length and the strength of the fibre matrix bond [Wall]. Long fibre lengths can be preserved at the cost of fibre matrix bonding. When the compounded fibre

reinforced material is subsequently injection moulded, great care is necessary if to retain the integrity of the long fibres and the advantages they offer in the cured product [Gibson]. However, in this programme each PF DMC was compression moulded. It was thought that the technique more readily permitted the preservation of the glass fibre length.

Flexural and impact strengths of moulding compounds covering the entire composition window are given in Tables 4.2 and 4.3. This data is illustrated graphically in Figures 4.41 and 4.42. The general trend is that flexural and impact strengths decrease with increasing filler content (in accordance with the results of the resin/filler mixtures described in Chapter 5.4). The lower the filler content, the stronger the compound. High levels of filler result in high dough viscosities which increase the amount of shear encountered by glass fibres in the extruder. This will result in filamentation followed by reduction of glass fibre length. Glass fibre bundles will remain partially intact when low filler loadings are used. High filler loadings filamentise and break down the glass fibres to a greater extent. This can be seen clearly in the SEM photomicrographs, Figs 4.44 and 4.45 (even when the different magnifications are taken into account). Complete filamentation exposes the individually surface treated filaments to the matrix to the full extent, thus making maximum use of the reinforcement. However, individual filaments are more prone to breakage, resulting in a reduced glass fibre aspect ratio. Partial filamentation means that the glass fibre filaments are not completely wetted out. However, the advantage is that glass fibre bundles are less prone to breakage. For every material and/or process there is a balance between achieving full wetting out on the one hand and maintaining glass fibre length on the other hand.

High levels of filler also reduce the degree of wetting and consequently result in weaker resin/filler and/or resin/glass fibre interfaces. A poorly wetted out system will allow less stress transfer across the interface and will invariably

have inferior mechanical properties. Figures 4.35, 4.36 and 4.37 illustrate the effect of filler loading on the appearance of moulding compounds. It can be seen from these photographs that a decrease in filler loading increases the degree of tackiness, the average glass fibre length and the extent to which the glass fibres are wetted out. Figures 4.37, 4.38 and 4.39 show that for a given filler loading, e.g. 60 phr of filler, the glass fibre content also affects the degree of wetting out. Increasing the glass fibre content from 10 to 30 wt% results in drier compounds. At a low filler loading, too low a fibre content will result in excessive flow of the resin/filler slurry. When on the other hand the glass fibre content is too high, e.g. 30 wt%, wetting out of the fibres becomes a problem. The fact that there is an optimum glass fibre content for a certain filler loading is also illustrated in the strength properties given in Figures 4.41 and 4.42. The consistency of a dough moulding compound, prior to compression moulding, containing 60 phr of filler (Polarite 102A) and 30 wt% glass fibre (Silenka 087) is illustrated in Figure 4.40.

Moulding compounds with low levels of filler contain relatively long glass fibre bundles which, along with the filler, are well wetted out. As the filler loading increases, the degree of wetting of fillers and glass fibres deteriorates and the average glass fibre length is reduced. When the resin content in the compound is low, i.e. when there is a high filler and/or glass fibre loading, the fillers will be wetted out better than the glass fibres. This is because resin and filler are mixed first and the glass fibre is introduced at a later stage near the diehead. So, there is relatively more resin available for filler wetting out than there is for wetting out of the glass fibres. This phenomenon is reflected in the flexural and impact strength results, where (in the case of Polarite 102A) there is a relatively large reduction in strength when the filler loading exceeds 100 phr. Different fillers will show this decrease in strength at different filler loadings, depending on their absorption characteristics, i.e. particle size, surface area (porosity) and surface chemistry. At filler loadings of 100 phr or more, the glass fibre content has little or no effect on flexural and impact strength. At relatively low filler loadings, i.e. less than 100 phr, there is an optimum glass fibre loading. Moulding compounds containing 20 wt% glass fibres have the highest flexural and impact strength. At higher fibre loadings, there is proportionally less resin/filler slurry available for glass fibre wetting out. The amount of slurry required for glass fibre wetting out also depends on the degree of filamentation of the glass fibres. The more filamentised the glass fibres become, the greater the glass fibre surface area. Besides resulting in an increase of the compound viscosity and consequently reducing the degree of wetting out, this will require larger quantities of slurry to maintain a good degree of wetting out.

At low levels of glass fibre content, e.g. 10 wt%, the matrix shows relatively large pores with a diameter of approximately 100  $\mu$ m (see SEM photomicrographs, Figures 4.46 and 4.47). These pores are approximately a factor of ten times larger than the glass fibre pull-out holes. As can be seen in SEM photomicrograph, Figure 4.46, cracks are formed linking these large pores (which act as stress concentrators). The pores in combination with the small amount of reinforcement are responsible for the inferior mechanical properties of these compounds.

As can be seen from Table 4.4 and Figure 4.43, the flexural modulus of the moulding compounds increases with increasing glass fibre and/or filler content. The effect of filler on the flexural modulus of phenolic resin has been discussed in Section 5.4.2. The addition of glass fibre to the resin/filler mixture increases the flexural modulus even further because the Young's modulus of glass fibre (E-type) is approximately ten times greater than that of cured phenolic resin.

Figure 4.57 shows a cured moulding compound containing 200 phr of filler (Polarite 102A) and 25 wt% glass fibre (Owens-Corning R52).

#### 5.5.2 Different Types of Glass Fibres

Three different types of glass fibre were investigated as potential reinforcements in moulding compounds. Two important factors need to be taken into account when considering a particular type of glass fibre, those of the glass fibre surface coating, i.e. sizing system containing a coupling agent, and bundle size. The surface coating supplies the key for interfacial bonding. Silane-based coupling agents are frequently used for this purpose. The coating system or sizing also serves to protect the glass fibres from filamentation and mechanical damage during transport and processing. The glass fibre bundle size gives an indication of the expected fibre integrity or degree of filamentation. The three types of glass fibre that were investigated all had silane-based sizing systems. Glass fibre manufacturers regard the precise composition of sizings as confidential information. General information about the glass fibres has been provided in Table 3.6.

The main differences between the three types of glass fibre are their bundle sizes and tendencies to filamentise. The different bundle sizes are as follows: Silenka 087 (120 tex), Vetrotex P223 (25 tex) and Owens-Corning R52 (67 tex). All fibres have been developed with the intention of chopped strand applications. Vetrotex P223 has a soluble size (in polyester resin) and filamentises very easily. The Owens-Corning R52 grade on the other hand has a low solubility in polyester resins and is designed for sheet moulding compounds. Silenka 087 glass fibres are treated with a 1 wt% of silane-based sizing which has been developed specifically for thermoplastics.

Tables 4.5, 4.6 and 4.7 illustrate the relative differences in flexural strength for moulding compounds containing the three types of glass fibres described above. This data is presented graphically in Figure 4.48. It can be seen that the Silenka 087 type of glass fibre is superior to the Owens-Corning R52 and Vetrotex P223 glass fibres. The flexural strength of Silenka 087 containing

compounds is consistently higher than the others. Silenka 087 has the largest bundle size of all three glass fibres. High glass fibre integrity results in comparatively small amounts of filamentation and/or fibre breakdown and hence a long fibre composite. The SEM photomicrograph, Figure 4.50, illustrates the long fibre nature of these compounds. Good fibre wetting out (see SEM photomicrograph, Figure 4.51) ensures efficient stress transfer. This good fibre wetting out is an unexpected bonus as the Silenka 087 silane system was originally designed for thermoplastics, polyamides in particular. Although more filamentation occurs at higher filler loadings, in relative terms, the Silenka 087 glass fibres maintain the highest fibre integrity. At a filler loading of 100 phr, Silenka 087 containing compounds with a glass fibre content of 20 to 40 wt % exhibit a minimum flexural strength of 100 MPa.

Both Vetrotex P223 and Owens-Corning R52 types of glass fibre had a silane based coating designed specifically for polyester sheet moulding compounds. Solubility of glass fibre sizings relates to polyester resins, or more specifically to the styrene solution in the polyester resin system. Therefore, the term solubility loses its relevance when used with water containing phenolic resin systems. A size which is soluble in a non-polar solvent such as styrene, is likely to be insoluble in a polar system (phenolic resin containing small amounts of water) and vice versa. Therefore, the extent to which the P223 and R52 glass fibre sizes are soluble in phenolic resins is the opposite when compared to polyester resins. SEM photomicrographs, Figs 4.52 and 4.53 demonstrate the different degrees of filamentation for both types of glass fibres. P223 which is more soluble in polyester systems, shows higher fibre integrity than R52, which has entirely filamentised. This explains the slightly superior flexural strength properties of Vetrotex P223 containing compounds compared to Owens-Corning R52 glass fibre filled systems. The impact strengths of the compounds containing the three different types of glass fibres are given in Tables 4.8, 4.9 and 4.10 and are presented graphically in Figure 4.49.

Silenka 087 containing compounds have superior impact properties, when compared with the other types of glass fibre. At a filler loading of 100 phr, Silenka 087 containing compounds have a higher impact strength than the compounds based on the other glass fibres have at a filler loading of only 60 phr. This is due to the superior fibre bundle integrity of the Silenka 087 glass fibres. Moulding compounds containing Vetrotex P223 and Owens-Corning R52 types of glass fibre have similar impact strengths. The impact strength value of the 30 wt% R52 reinforced compound with 140 phr filler is higher than expected. The amount of shear encountered by the glass fibres in the extruder increases with increased filler loading. Differences in fibre integrity between the R52 and P223 types of glass fibres and their effect on the flexural and impact strength results are therefore reflected to a greater extent at higher filler loadings. Ignoring the impact strength value at 140 phr filler, P223 has a marginally higher impact strength than R52 containing moulding compounds.

Work done by Burns showed that flexural strength decreased while impact strength increased with increasing bundle tex. The results obtained in this work showed that both flexural and impact strengths are highest when a high bundle tex glass fibre, i.e. Silenka 087, is used. However, the work carried out by Burns relates to chopped strands in sheet moulding compounds (SMCs). In this work, glass fibres were passed through an extruder rather than being placed on a resin/filler slurry. Therefore, compared to an SMC application, a low bundle tex glass fibre will be damaged, filamentised and further broken down to a much greater extent when passed through the twin screw compounder. Due to the high shear environment in a co-rotating twin screw extruder, filamentation of a glass fibre is immediately followed by severe fibre damage resulting in a substantially reduced average glass fibre length. The flexural modulus results are given in Tables 4.11, 4.12 and 4.13. All three types of glass fibre increase the flexural modulus. The extent to which the flexural modulus increases is different for each type of glass fibre. However, it seems that there is no consistent trend as to how the different types of glass fibre affect flexural modulus. As the glass fibre content increases from 20 to 30 wt%, the relative differences of flexural modulus between the three types of glass fibre are entirely different.

#### 5.5.3 Extruder Output

Maintaining a certain moulding compound composition whilst increasing the extruder output has an effect on the flexural and impact properties of the compounds that are being produced (see Table 4.14). A higher extruder output required an increase in screw speed. A higher screw speed implies more shear and consequently more fibre breakdown is expected, combined with improved wetting. The extruder barrel was cooled in order to offset any increase in temperature due to shear heating. Flexural and impact strengths decrease as the extruder output increases from 100 to 150 gr/min. It seems that the higher levels of shear and their effect on glass fibre length offset any improvement in properties as a result of better wetting. The effect of extruder output rate on flexural modulus is unclear.

#### 5.5.4 Different Types of Fillers

#### 5.5.4.1 Mica

The effects of mica/Polarite 102A 50/50 filler mixtures and pure mica on the mechanical properties of moulding compounds have been investigated (see Tables 4.15, 4.16 and 4.17). These results show that increasing the filler level of mica containing compounds does not significantly alter their flexural strength. In comparison, the flexural strength of Polarite 102A based compounds is halved over the same filler loading range. Surprisingly, mica/Polarite 102A filler mixtures have flexural strength and modulus values lower than either Polarite

102A or mica alone containing compounds. It can be seen in the SEM photomicrograph, Figure 4.54, that, as a result of the flake-like shape of mica, the glass fibre bundles have been filamentised to a large extent. However, the consequences of this reduction in glass fibre bundle integrity, are not reflected in the impact strength of mica containing compounds. On the contrary, at high filler loadings (140 phr), mica based compounds have a higher impact strength than Polarite 102A containing compounds. Figure 4.58 shows a moulding containing 140 phr mica and 20 wt% Owens-Corning R52.

#### 5.5.4.2 Clay/cellulose filler mixtures

Two mixtures of clay and cellulose, i.e. clay/cellulose 70/30 and 30/70, have been investigated as potential fillers (see Tables 4.18, 4.19 and 4.20).

In traditional phenolic moulding compounds, cellulose fillers are widely used to reduce shrinkage during cure, to improve impact strength and to provide flow control [Knop and Pilato]. Their detrimental effect on fire performance (as a result of their organic nature) limits the extent to which they can be used as fillers in state of the art fire retardant phenolic moulding compounds. In this work, cellulose based fillers have been included for completeness.

It was found that cellulose fillers have very different absorption characteristics compared to mineral fillers. Addition of 20 phr of clay/cellulose 30/70 filler is sufficient to increase the viscosity to such an extent that extrusion of the compound becomes possible. Mineral filled systems require at least double the amount of filler in order to produce a moulding compound that is extrudable. The higher the cellulose content in the filler system, the higher the viscosity. It is because of these viscosity considerations that the clay/cellulose 70/30 filled compounds do not cover the same composition range as the 30/70 filler based systems.

The flexural modulus results are quite inconsistent; the reason for this is unclear. The flexural strength properties at 60 phr filler are comparable to compounds containing a mineral filler (Polarite 102A) at the same filler loading. The compound containing only 20 phr of 30/70 filler has a relatively high flexural strength, i.e. 99 MPa, and an excellent impact strength, higher than any other compound that has been investigated. The high impact strength is quite surprising as that particular compound contains over 70 wt% of phenolic resin. Most other fillers would not allow this compound to be compression moulded without having large pores in the cured sample and/or giving excessive amounts of flash. An example of a compression moulded sample containing 40 phr of clay/cellulose 30/70 filler and 15 wt% Owens-Corning R52 is given in Figure 4.59. The relatively poor degree of wetting out of the Owens-Corning R52 type of glass fibre by clay/cellulose 70/30 filled phenolic resin is illustrated in the SEM photograph, Figure 4.55. This is reflected in the poor flexural and impact strengths of this particular moulding compound.

# CHAPTER 6 CONCLUSIONS

The main aim of this work was to develop simple, long fibre phenolformaldehyde dough moulding compounds (PF.DMC), based on heat curable phenolic resol resin, mineral filler and glass fibre.

After establishing the compounding parameters, several minerals were investigated as potential fillers for phenolic DMCs. Resin/filler mixtures were prepared using either a co-rotating twin screw extruder or a Z-blade mixer. Viscosities of the uncured samples were measured, followed by measurement of the flexural and impact properties of the cured samples.

Subsequently, PF.DMCs covering wide filler loading and glass fibre content ranges were prepared using a co-rotating twin screw compounder. The effects of extruder output and different types of glass fibres and fillers on mechanical properties were investigated.

The conclusions drawn from this work are grouped under the following headings: processing (compounding and moulding), resins, fillers and resin/filler/glass fibre moulding compounds.

#### 1. Processing

- 1.1 Compounding J2040L and filler in a twin screw compounder at a higher temperature results in lower torque levels than does compounding at lower temperatures and the cured samples have a higher density and superior flexural strength.
- 1.2 The screw speed in a twin screw compounder has been shown to have no effect on the viscosity of J2027L/filler mixtures.

- 1.3 Increasing the twin screw compounder output reduces the flexural and impact strengths of moulding compounds.
- 1.4 Addition of 2 parts of internal release agent based on a calcium-soap (TR 016) to 100 parts of filler results in satisfactory release properties following compression moulding.

#### 2. Resins

- 2.1 Adding small amounts of low viscosity (J2027L) to high viscosity (J2040L) phenolic resin results in a substantially reduced overall viscosity.
- 2.2 High viscosity resin (J2040L) has approximately the same viscosity at 50°C as the low viscosity (J2027L) resin at 20°C.

#### 3. Fillers

- 3.1 Adding a particulate filler to a phenolic resin usually decreases the flexural and impact strengths. Flexural modulus increases with increased filler loading.
- 3.2 J2040L/filler mixtures show an increase in viscosity and flexural modulus as the average filler particle size decreases. In the case of untreated fillers, decreases in flexural and impact strengths are observed.
- 3.3 Mixtures of J2040L with an aminosilane treated china clay (Polarite 102A) have higher viscosities and superior flexural and impact properties compared to untreated china clay (PoleStar 200R and Devolite) filled systems.
- 3.4 Mixtures of J2040L and calcium carbonate with a fatty acid surface coating have lower viscosities than untreated calcium carbonate filled systems.

- 3.5 Mixtures of J2040L and Polarite 420EW (a calcium carbonate with a polymeric coating) have inferior mechanical properties compared to other calcium carbonate filled systems.
- 3.6 Mixing J2040L and 70 wt % of "small" Polarite 102A with 30 wt % of "large" dolomite filler particles results in mixtures with a lower viscosity than any other Polarite 102A/dolomite filler combination filled system.
- 3.7 J2040L/dolomite mixtures containing more than 80 phr of filler show a decrease in both flexural and impact strength of about 50%.
- 3.8 Replacing half of Polarite 102A with dolomite reduces the overall viscosity of the mixture by nearly a factor of ten.
- 3.9 Both flexural and impact strength are not altered significantly by replacing china clay with different amounts of aluminium trihydrate. Adding ATH to china clay filled systems reduces the overall viscosity.
- 3.10 Adding wollastonite to china clay filled systems lowers the overall viscosity.

#### 4. Resin/filler/glass fibre moulding compounds

- 4.1 Long fibre dough moulding compounds covering wide filler loading and glass fibre content ranges can be produced using a co-rotating twin screw compounder.
- 4.2 Moulding compounds with high levels of filler loading suffer a substantial degree of glass fibre breakdown during compounding.
- 4.3 Moulding compounds containing Silenka 087 glass fibres have superior flexural and impact strengths compared to ones containing Owens-Corning R52 or Vetrotex P223 glass fibres.

- 4.4 Mica containing moulding compounds maintain their flexural strength with increased filler loading.
- 4.5 Moulding compounds containing clay/cellulose 30/70 as filler have superior impact properties, compared to china clay filled compounds.

## CHAPTER 7

## FUTURE WORK RECOMMENDATIONS

- 1. To study the effects of a wide range of fillers on the viscosities and mechanical properties of phenolic resins.
- 2. To carry out a detailed study of the exact failure mechanisms for the different resin/filler mixtures.
- 3. To investigate the use of a twin screw compounder for the production of unsaturated polyester resin, phenolic novolac and epoxy based moulding compounds.
- 4. To control the glass fibre orientation to a greater extent, without compromising the glass fibre length.
- 5. To study the effect of partially, or entirely, replacing the glass fibre continuous roving by chopped strand glass fibres, using a force feed hopper, on the properties of phenolic moulding compounds.
- 6. To study the effects of different fillers and compound compositions on the fire retardancy of phenolic moulding compounds.

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# APPENDIX TABLES OF GRAPHS

- Appendix A-1: Data of Figure 4.1: the effect of temperature on the viscosity of J2040L
- Appendix A-2: Data of Figure 4.2: viscosity of J2040L/Polarite 102A mixture at 20° and 50°C
- Appendix A-3: Data of Figure 4.3: effect of compounding temperature on torque
- Appendix A-4: Data of Figures 4.4 and 4.5: effect of compounding temperature on flexural strength and modulus
- Appendix A-5: Data of Figure 4.6: effect of compounding temperature on bulk density
- Appendix A-6: Data of Figure 4.7: effect of screw speed on viscosity
- Appendix A-7: Data of Figure 4.8: mixtures of J2040L/J2027L: effect of viscosity
- Appendix A-8: Data of Figure 4.9: effect of resin type on viscosities of resin/PoleStar 200R mixtures
- Appendix A-9: Data of Figures 4.10, 4.18 and 4.22: viscosity of china clay/dolomite systems
- Appendix A-10: Data of Figures 4.11, 4.19 and 4.23: flexural strength of china clay/dolomite systems
- Appendix A-11: Data of Figures 4.12, 4.20 and 4.24: impact strength of china clay/dolomite systems
- Appendix A-12: Data of Figures 4.13, 4.21 and 4.25: flexural modulus of china clay/dolomite systems
- Appendix A-13: Data of Figures 4.14, 4.26 and 4.30: viscosity of calcium carbonate, PoleStar 200R/ATH and Polarite 102A/ wollastonite systems

Appendix

Appendix A-14:	Data of Figures 4.15, 4.17 and 4.31: flexural strength of
	calcium carbonate, PoleStar 200R/ATH and Polarite 102A/
	wollastonite systems

- Appendix A-15: Data of Figures 4.16, 4.28 and 4.32: impact strength of calcium carbonate, PoleStar 200R/ATH and Polarite 102A/ wollastonite systems
- Appendix A-16: Data of Figures 4.17, 4.29 and 4.33: flexural modulus of calcium carbonate, PoleStar 200R/ATH and Polarite 102A/ wollastonite systems

The appendices that contain the results of flexural and impact tests give three values for each filler loading, i.e. the lowest value, the average value and the highest value.

		Viscosity (mPa.s)		
Temperature (°C)	,	Shear rate (s <sup>-1</sup> )		
	5.41	10.82	21.64	
21	10466	11104	-	
26	6251	6251	6374	
31	3784	3866	3989	
41	1727	1645	1666	l
51	-	640	802	

#### APPENDIX A-1: The effect of temperature on the viscosity of J2040L

### APPENDIX A-2:

Viscosity of J2040L/Polarite 102A mixtures at 20° and 50°C

Shear rate =  $6 \text{ s}^{-1}$ 

Filler loading	Viscosity	(mPa.s)
(phr)	Tempera	iture (°C)
	20	50
40	170	50
57	334	75
80	980	121

	Torqu	e (%)	
Filler loading (phr)	Temperature (°C)		
·	20	50	
204	12.5	•	
252	• •	11	
274	18	-	
296	-	13	
313	20	•	
333	-	16	
554	-	21	

## APPENDIX A-3: Effect of compounding temperature on torque

# APPENDIX A.4:

# Effect of compounding temperature on flexural strength and modulus

	Flexural strength (MPa)		Flexural modulus (GPa)	
Filler Ioading	Temperature		Temperature	
(phr)	20	50	20	50
204	5.89	-	4.26	-
252 274	- 6.45	6.77	8.70	5.65
275	6.61	-	8.76	-
296	-	9.02	-	14.31
313	8.42	-	10.13	-
333	-	8.59	-	13.63
554	-	6.62	-	) 10.14

	Bulk dens	ity (g/cm³)
Filler	Tempera	iture (°C)
(phr)	20	50
204	1.35	-
252	-	1.53
274	1.41	-
275	1.47	-
296	-	1.58
313	1.56	-
333	-	1.64
554	-	1.85
1		

APPENDIX A-5: Effect of compounding temperature on bulk density

APPENDIX A-6: Effect of screw speed on viscosity

Resin = J2027L Shear rate = 24 s<sup>-1</sup>

Filler	Viscosity (mPa.s)				
loading (phr)	Screw speed (rpm)				
	100	150	225	300	400
42	16	-	-	-	
47	-	-	21	-	-
49	-	-	-	-	20
51	-	21	-	-	-
69	-	29	-	-	-
70	-	-	31	31	-
73	26	-	-	-	-
84	-		-	-	50
87	-	52	-	-	-
88	55	-	-	-	-
96	-	-	50	-	-
100	-	-	-	97	-
113	-	-	-	121	-
119	-	70	-	-	-
121	-	-	73	-	-
123	-	-	-	-	153
137	<b>-</b> .	-	222	-	-
146	-	-		160	-
151	1 -	-		-	327
168	-	-		-	336

wt %	Viscosity (Pa.s)		
J2027L	As measured	Rule of mixtures	
0.0	26.9	26.9	
2.5	23.3	26.3	
5.0	21.5	25.6	
7.5	19.3	25.0	
10.0	16.1	24.3	
20.0	10.7	21.7	
50.0	2.9	13.8	
100.0	0.6	0.6	

APPENDIX A-7: Mixtures of J2040L/J2027L: effect of viscosity (20°C)

APPENDIX A-8: Effect of resin type on viscosities of resin/PoleStar 200R mixtures

	Viscosity	(mPa.s)
Filler loading	Resin type	
(phr)	J2027L	J2040L
50	21	-
67	35	-
96	194	1294
113	-	2325
116	405	-
126	-	3905
131	-	4331
134	554	4580

Shear rate: J2027L/filler mixture: 24 s<sup>-1</sup> J2040L/filler mixture: 1.2 s<sup>-1</sup>

.
Filler	Viscosity (Pa.s)												
loading (phr)		Polarite	102A/dolomite	· · · ·	Devolite	/dolomite	PoleStar 20	0R/dolomite	Dolomite				
	100/0	70/30	50/50	30/70	100/0	50/50	100/0	50/50					
40 46	170	85											
49 52 57	394		67				] 		82				
66 69		153							142				
71 75 76			142	107		128							
77 79								149	195				
80 86 88	980	426							320				
90 92			308	170	427		1294	 					
96 97		625				234							
100 104 108	3142		, ,	270				359					
111 112			500			419	2325						
113 116 120			362					817	1544 2059				
125 126				504			3905 4580						
132 134	5343							·					
137 138 148	5822	3923			2692								
167 168 190			3071 3923		5195								
224 233			6337 6710										

### APPENDIX A-10:

Filler		<u> </u>		Flexu	ural Strength (MPa)					
Loading (phr)		Polarite/102/	Vdolomite		Devolite/	dolomite	PoleStar 20	0R/dolomite	Dolomite	
(1)	100/0	70/30	50/50	30/70	100/0	50/50	100/0	50/0	-	
40 46 49 52	32.0/40.0/44.2	40.4/41.2/42.1	35.0/37.7/40.6						35.7/36.7/40.5	
57 59 62 66	32.0/25.0/28.9	36.3/37.4/38.5			15.6/16.4/17.2		17.6/18.7/20.6		20 2/40 4/41 7	
69 71 75 76 77 79 80 83 83 86			36.4/41.0/45.6	33.4/34.8/37.2	31.1/33.8/36.5	12 8/14 5/15 6		22.7/25 3/29 7		
	22.7/25.0/27.4				18.9/19.9/20.8		12.011.010.0	10.7/11.3/12.6	15.4/18.1/20.9	
88 92 94 95		35.2/36.1/37.0	36.0/37.9/39.7	26.9/30.8/34.9			13.8/16.5/19.2			
96 97 100	51.9/53.2/54.5		25.4/33.8/43.8		18.0/20.5/24.0	10.8/12.3/13.2		12.6/13.7/14.9		
104 110 111 112 113 116 120 125 134 147 148 167	43.1/49.8/56.6			27.1/30.0/33.2		9.8/10.8/11.4	16.9/19.5/21,4			
			27.9/33.5/36.4	30.0/30.6/31.3				10.1/10.4/11.3	20.3/20.4/20.6 17.4/18.1/18.8 17.2/19.8/23.0	
		30.8/34.6/42.3	28.5/32.7/37.0							

# APPENDIX A-11:

Filler	Impact Strength (N/mm <sup>2</sup> )													
Loading (phr)		Polarite/102	A/dolomite		Devolite/	/dolomite	PoleStar 20	0R/dolomite	Dolomite					
	100/0	70/30	50/50	30/70	100/0	50/50	100/0	50/50	-					
40 46 49	2.3/3.5/4.4	2.7/3.5/3.9	3.2/3.9/4.6						3.2/3.6/3.8					
52 57 59 62	2.8/3.5/4.1		i		2,9/3.2/3.5									
66 69 71		3.0/3.4/4.1	0.000.000.0	3.1/3.5/3.9	2 1/2 4/4 0		2.7/3.3/3.9		3.1/4.0/4.6					
75 76 77 79			2.0/3.0/3.9	:	3. 1/3.4/4.0	1.6/1.9/2.3	2.2/2.4/2.9	1.2/1.4/1.5	2.0/2.2/2.3					
80 83 86	3.9/4.6/4.9				3.6/3.7/3.8				1.0/1.3/1.5					
88 92 94 95		2.8/3.0/3.3	2.8/3.1/3.6	3.0/3.2/3.6	2.2/2.6/3.0		2.5/2.9/3.1							
96 97 100	3.7/4.5/5.0	3.2/3.5/4.0				1.1/1.2/1.3		1 0/1 0/1 1						
104 110 111				2.8/3.2/3.8	2.7/2.8/2.8	1.3/1.4/1.5		1.0/1.0/1.1						
112 113 116 119	3.4/4.1/4.9		2.6/3.5/4.3		2.2/2.5/3.1		2.1/2.2/2.3							
120 125 131				0.1/0.0/0.6			2.4/2.6/3.1	1.2/1.3/1.4	1.3/1.5/1.8 1.8/1.8/1.8					
134 135 147 148		1. 1/1.3/1.5		<i>د</i> , ۵۵.۷/۵,۵	2.7/2.8/2.9				1.8/2.1/2.4					

### APPENDIX A-12:

Filler		Flexural Modulus (GPa)													
Loading (phr)		Polarite/102	A/dolomite		Devolite	/dolomite	PoleStar 20	0R/dolomite	Dolomite						
"	100/0	70/30	50/50	30/70	100/0	50/50	100/0	50/0	-						
40 46 49 52	7.8/8.0/8.7	7.0/7.9/8.8	6.6/7.0/7.8						6 1/6 4/6 0						
57 59 62 66	7.3/0.1/0.0	8.6/9.2/9.7			6.1/6.7/7.4		5.3/6.1/6.8		7 5/7 6/8 2						
71 75 76 77			8.2/9.8/11.3	6.0/7.1/7.6		8.2/8.7/9.3	8.8/9.5/10.4		6 3/7 0/7 3						
79 80 83	11.0/11.5/12.0				8.0/8.3/8.7			2.1/2.5/3.1	84/93/106						
88 92 94		9.5/9.8/10.2	8 2/9 0/9 9	5.5/6.1/6.4			9.5/9.9/10.2								
96 97 100	12.5/12.7/13.0	7.3/7.9/8.9				4.3/5.2/6.3		4.9/5.4/6.0							
110 111 112 113	13 3/13 4/13 5			8.6/9.6/11.2	9.4/9.9/10.3	6.4/6.9/7.8	12.0/13 6/11.4								
116 120 125 134	10.010.410.0		7.4/7.8/8.8	8,1/9.9/11.8				5.5/5.9/6.3	8.8/8.9/9.0 11.7/12.8/13.9						
147 148 167		16.1/16.7/17.5	10.8/11.8/12.7						15.2/16.9/19.4						

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### APPENDIX A-13:

Filler Loading (pbr)	Calcium Carbonate				PoleStar	Polarite 102A	Wolllastonit e		
(piii)	Albarex	Britomya	Omya	100/0	70/30	50/50	30/70	100/0	60/40
40 57 80 108 113 126 131 132 134				2325 3905 4331 4580				170 334 980 3142 5343	
134 137 155 170 172 177 181	263	650			4899	2308		5822	3887 4402
190 194 202 204 243 272 291	401 471	912	2423 2432			x	4100		

## APPENDIX A-14:

Filler	. <u></u>	- <u></u> <u>-</u> <u>-</u>	<u>_</u>	- <u></u>	FI	exural Strength (MP	a)	<u></u>	<u></u>		
Loading (obr)		Calcium Ca	rbonates	· • •		PoleStar 20	OR/ATH	Polarite 102A/Wollastonite			
(p)"/	Albarex	Britomya	Omya	Polarite 420EW	100/0	70/30	50/50	30/70	100/0	80/20	60/40
40 57 62 77 80 94 96 113 155 170 172 179 181 190 194 204 243 252 272 291 296 333	14.3/14.7/15.2 12.7/15.2/17.0	20.8/22.8/24.1 14.3/15.3/15.9	19.4/21.9/24.0 21.7/23.4/25.1	6.0/6.8/7.7 8.5/9.0/9.3 8.3/8.6/9.1	17.6/18.7/20.6 12.8/14.6/15.6 13.8/16.5/19.2 18.9/19.5/21.4	19.3/20.1/22.6	20.9/23.4/25.9 12.0/15.5/17.3	20.8/21.7/22.5	32.0/40.0/44.2 25.0/28.9/32 22.7/25.0/27.4 51.9/53.2/54.5 43.1/49.8/56.5	22.8/24.5/28.0	26.2/29.9/35.2

Filler					Impact Strength (N/mm²)							
Loading (obr)		Calcium Ca	rbonates			PoleStar 20	OR/ATH	Polarite 102A/Wollastonite				
(p)	Albarex	Britomya	Omya	Polarite 420EW	100/0	70/30	50/50	30/70	100/0	80/20	260/40	
40 57 62 77 80 94 96 113 131 155 170 172 179 181 190 194 202 204 243 252 272 291 296	2.1/2.2/2.3 2.6/2.7/2.8 1.9/2.3/2.8	2.3/2.4/2.5 2.6/2.7/2.8	1.9/1.9/2.1 2.2/2.3/2.3	1.1/1.1/1.1 1.1/1.2/1.3 1.4/1.5/1.8	2.7/3.3/3.9 2.2/2.4/2.9 2.5/2.9/3.1 2.1/2.2/2.3 2.4/2.6/3.1	1.5/1.8/2.4	1.9/2.3/2.5 1.6/1.9/2.1	2.4/2.4/2.5	2.3/3.5/4.4 2.8/3.5/4.1 3.9/4.6/4.9 3.7/4.5/5.0 3.4/4.1/4.9	2.1/2.2/2.3	2.4/2.5/2.5	

#### APPENDIX A-15:

APPENDIX A-16:

	Flexural Modulus (GPa)													
Filler		Calcium C	arbonates		<u> </u>	PoleStar 20	DOR/ATH	Polarite 102A/Wollastonite						
Loading (phr)	Alborex	Britomy	Omya	Polarite 420EW	100/0	70/30	50/50	30/70	100/0	80/20	60/40			
40 57 62 77 80 94 96 113 155 170 172 179 181 190 194 204 243 252 272 291 296 333	6.6/7.0/7.4 7.1/7.9/8.8	13.1/14.1/15.0 15.4/15.6/15.9	15.3/16.3/17.3 15.8/16.2/16.5	4.9/5.7/6.7 13.2/14.3/15.4 12.7/13.6/14.5	5,3/6.1/6.8 8,8/9.5/10.4 9.5/9.9/10.2 12.0/13.6/11.4	12.3/14.7/16.1	13.1/13.6/14.1 16.0/16.7/16.8	13.3/13.8/14.1	7.8/8.0/8.7 7.3/8.1/8.8 11.0/11.5/12.0 12.5/12.7/13.0 13.3/13.4/13.5	19.6/21.0/22.9	20.7/21.4/21.8			