

CHAPTER 4 COMPOUNDING TECHNIQUES

The mixing of fillers, wax and resin to produce a desired polymer product is called *compounding*. The polymer and filler are mixed, melted and pelletised for further application. The equipment used for compounding includes single-screw extruders, intermeshing twin-screw extruders, two-roll mills and continuous mixers. A continuous mixer consists of a single-screw extruder for pumping and a short, non-intermeshing, counter-rotating, twin-screw extruder for mixing and melting.

The type of compounding required depends on the type of mixing to be done. Polymers form a matrix or a continuous phase. The additional component forms a dispersed phase embedded into the polymer matrix during mixing. The mixing can occur by three mechanisms, namely distributive, dispersive and molecular interdiffusion (Chung *et al*, 2004).

Distributive mixing increases the interfacial area between the polymer matrix and the dispersed phase. Distributive mixing improves the spatial distribution without cohesive resistance; it is also called "simple or extensive mixing". *Dispersive mixing* reduces the particle sizes of the additional component. For this to occur, the cohesive resistance has to be overcome to achieve finer levels of dispersion. Dispersive mixing is also called "intensive mixing". Generally, dispersive mixing results in distribution. But distribution may also occur without dispersive mixing. Figure 9 depicts distributive and dispersive mixing.

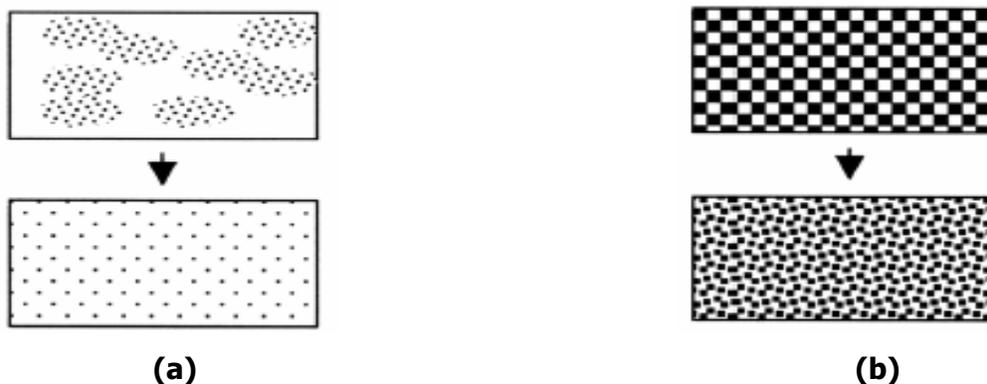


Figure 9: Two types of mixing mechanism: (a) distributive mixing, and (b) dispersive mixing (Chung *et al*, 2004).

If the additional component and the polymer are miscible, molecular interdiffusion occurs in addition to distributive and dispersive mixing. The molecule of the additional component diffuses into the polymer matrix and the polymer diffuses into the dispersed phase. Figure 10 shows the mechanism of molecular interdiffusion.

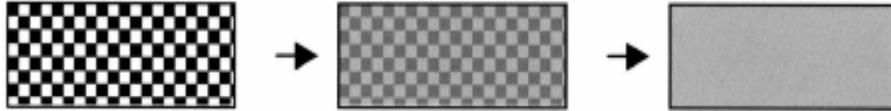


Figure 10: Mixing mechanism: molecular interdiffusion

The molecular interdiffusion increases with an increase in temperature. The time to reach a final composition is inversely proportional to the temperature. At a high temperature, it will take a long time for the polymer matrix and the dispersed component to form a final composition (Chung *et al*, 2004).

Types of flow

The two types of flow in compounding are the *shear flow* and the *elongation flow*, which is also known as the "stretching or extension flow".

Shear and elongation flow

Shear flow occurs when there is a pressure drop along a flow path. Elongation flow occurs when there is compression associated with stress. Equations 4 and 5 illustrate shear and elongation flow using the Trouton relationship (Rauwendaal, 1981).

$$F_{\text{SHEAR}} = 3\pi\eta\dot{\gamma}r_1r_2 \quad (4)$$

$$F_{\text{ELONGATION}} = 3\pi\eta\dot{\varepsilon}r_1r_2 \quad (5)$$

Where η is the viscosity, $\dot{\gamma}$ is the shear rate, $\dot{\varepsilon}$ the elongation rate, and r is the radius of a particle.

Polymer melts are highly viscous and for this reason laminar flow is common, which causes inequality in distribution. Polymer melts therefore need to be re-orientated to attain uniform distribution. Stress develops if a polymer melt is sheared or elongated. The polymer melt varies linearly with the rate of shear stress at a given time.

Distributive mixing occurs at a low shear rate. However, dispersive mixing can occur only at shear rates great enough to break up the dispersed phase.

Simple shear flow depends on the velocity gradient (γ') perpendicular to the main flow direction. This gives rise to a shear stress (τ) (Newton's viscosity law).

Above a certain Weber number value the droplets break as shear forms the droplet. The Weber number is a dimensional ratio of the shear force to surface tension forces:

$$We = \frac{\eta \gamma' d}{\sigma} \tag{6}$$

Where d is the droplet diameter, σ is the interfacial tension, γ' is the shear rate and η is the viscosity.

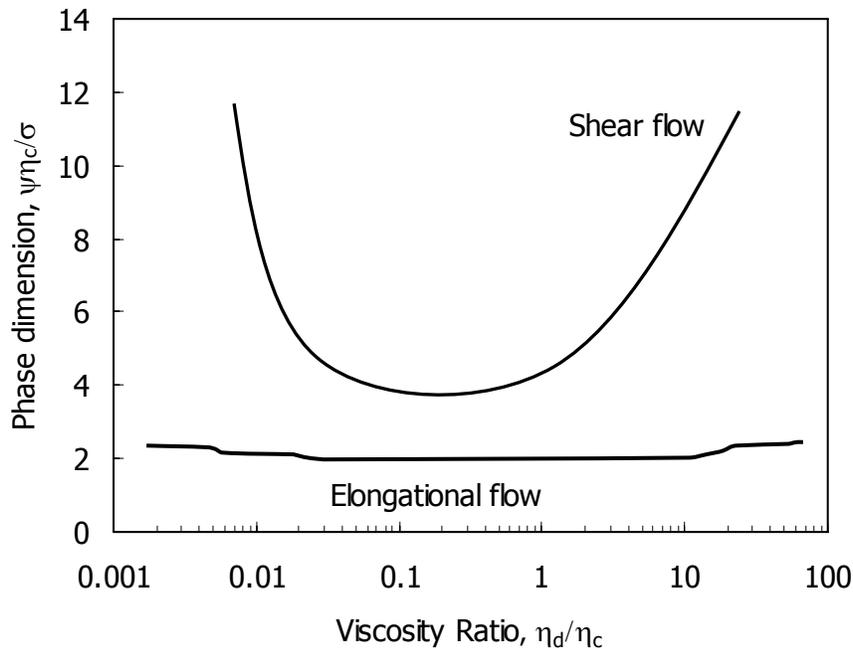


Figure 11: Schematic representation of the phase dimension of an immiscible fluid as a function of the viscosity ratio (Karam and Bellinger, 1968).

As the Weber number exceeds a critical value, droplet break-up occurs. The drop in viscosity to that of the continuous phase determines the critical Weber number. This is depicted in Figure 11, which clearly shows that the droplet diameter (d) can be reduced if the interfacial tension (σ) is lowered, the shear rate ($\dot{\gamma}$) is increased and when the viscosity of the dispersed phase (η_d) is similar to or slightly lower than the viscosity of the continuous phase (η_c). Theory predicts that above a viscosity ratio of 4, the break-up of droplets will not occur. This occurs with slightly higher viscosity ratios. For high drop viscosities, any slight deformation will cause droplet rotation, thereby preventing break-up (Karam and Bellinger, 1968).

There is a velocity gradient in the direction of the key flow in elongation flow. As there is no transverse shear component is not present, droplet rotation is not possible and very viscous drops can be deformed.

4.1 Batch mixers

Open mill

This class consists of two-roll or three-roll open mills. A two-roll mill consists of two counter-rotating rolls that can be adjusted to move closer to each other. The nip is the distance of closest approach between the two rolls. In this type of compounding, extensive elongation mixing occurs due to the extentional flow that takes place at between the rolls (Swanborough, 1979). Mixing in the axial direction must be aided by repeated “folding over” of the mass on the mill for good mixing.

Advantages of the two-roll mill

- There is good temperature control of the product since there is cooling and heating.
- There is also a greater surface area available to the polymer system.
- The region of high shear is minimal; this avoids temperature build-up.
- The degree of dispersive mixing is high.

Disadvantages of the two-roll mill

- The process is dirty and it is not easy to achieve a uniform product.
- The process takes a long time.

- It operates as an open system, which implies contact with air at high temperatures.
- Temperatures fluctuate when fillers and other materials are added (Brichall *et al.*, 1981).

Internal mixers

An internal mixing process is similar to an open mill compounding process, but it is enclosed in a mixing chamber. Three types of mixing process occur. Firstly, an intensive or dispersive mixing occurs around the tips of the rotor blade. Extensive mixing then occurs due to the shear flow and takes place between the cylindrical portion of the rotor and the chamber wall; and finally distributive mixing due to random plug convection between the two rotor tips (Hold, 1982).

The advantages of internal mixers are the versatility and simplicity of operation, and the robustness of the machines. The disadvantages include high capital cost, poor temperature control and high and uneven power load.

4.2 Continuous compounders

To meet the requirements for high throughput capacities and high quality product standards, compounding equipment has been developed, ranging from a single-screw extruder to a twin-screw extruder (Mack, 1980).

Conventional single-screw extruder

A single-screw extruder uses a combination of pressure and drag flow to pump polymer material. A conventional single-screw extruder melts and pumps material against pressure (Hold, 1982). A single-screw extruder can compound and mix because of the shear force, which moves the material through the screw channels. However, it is not a good mixer because the material that passes through the extruder is subjected to the shearing only, i.e. there is no elongational flow (Tadmor, 1970). The main advantages and disadvantages of single-screw extruders are:

Advantages of the conventional single-screw extruder

Mechanically simple, easy to operate and capable of high-pressure generation.

Disadvantages of the conventional single-screw extruder

Lack of positive transmission characteristics, inadequate compounding and homogenising capabilities.

Twin-screw extruders

The development of twin-screw extruders emerged from the limitations of single-screw extruders. There are two types, namely intermeshing and non-intermeshing extruders. Each type is further divided according to the direction in which screw rotates; it can be by co-rotational or counter-rotational. Figure 12 shows the different types of twin-screw extruder.

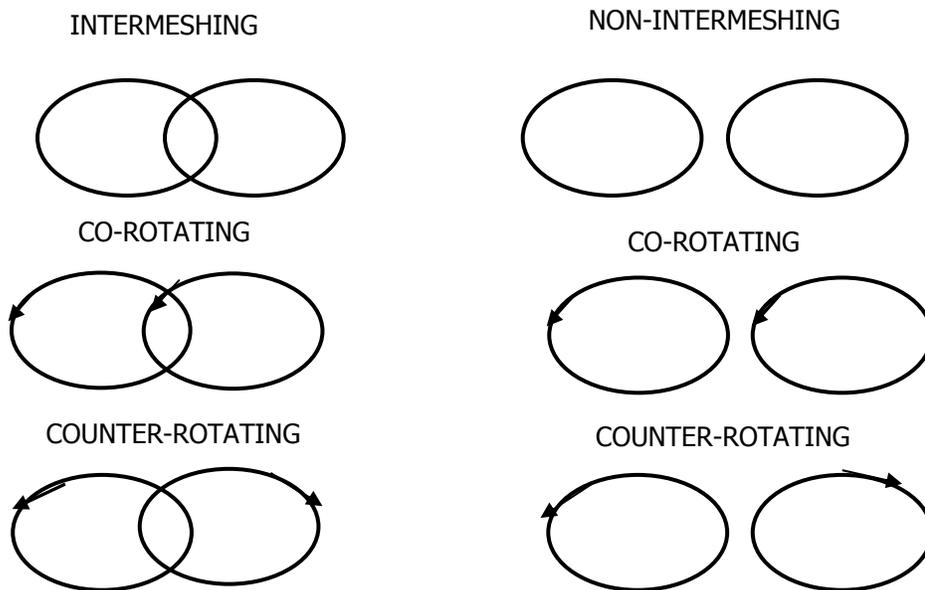


Figure 12: Typical types of twin-screw extruder (Shenoy, 1999)

Intermeshing co-rotating extruders

This type of conventional extruder is associated with positive displacement and is effectively self-wiping if kneader blocks are used (Jakopin, 1974). The co-rotation of the screws moves the material back and forth between the screws, thus allowing effective dispersive mixing (Rauwendaal, 1981). By selecting different numbers of flights, the intensity of the shearing

action can be changed. Special shearing can be arranged between screw sections to perform intensive dispersive mixing.

Advantages of twin-screw extruders

- Positive displacement gives throughput without affecting the properties of the product being processed (Rauwendaal, 1981).
- The self-wiping characteristics mean that no material is left in the machines.

Disadvantages of twin-screw extruders

- High capital cost.
- Mechanically complicated and difficult to make.

Intermeshing counter-rotating extruders

These are similar to co-rotating twin-screw extruders since both of them give positive displacement. The intermeshing point of the counter-rotating screws acts as a “calendar nip”. A small portion of material passes through the nip between the screws, while the remainder passes along the axes in closed chambers (Nichols, 1982). The residence time in an intermeshing counter-current extruder is short and therefore it is sensitive to thermal degradation of the material.

Non-intermeshing counter-rotating extruders

These are composed of two screws rotating at a given speed in different directions. The flight of one screw does not protrude into the channel of other screw; therefore this extruder is similar to a single-screw extruder, with the exception of having two screws. Because the stream of flow meets at the interface between the screws, there is more extensive mixing than in a single-screw extruder. Staging the flight of the screws can further increase extensive mixing, but this does reduce the pumping efficiency (Shenoy, 1999). Non-intermeshing counter-rotating is used only where dispersive mixing is not a necessity (Walk, 1982). Non-intermeshing counter-rotating extruders are commonly used in polymer blending, preparation of pigment concentrates, adhesives and fibreglass reinforcement.

Continuous internal mixers

Continuous internal mixers are designed to control the forward action of material through the mixer and the mixing action independently (Hold, 1982). They are composed of two sections: the mixer itself and an intensive mixing section. The mixer has a conveying section that propels the material forward and another section that moves the material in the opposite direction for intensive mixing. In the intensive mixing section, the material is dispersed through the gaps between the rotor and the chamber walls, coupled with a kneading action between the material itself and the rotor. The shear deformation and distribution that takes place within the residence time is greater in a continuous internal mixer with a non-intermeshing mixing blade than in any twin-screw extruder. The material has to be fed continuously because mixing along the axes is not effective. Since this type of compounder does not produce enough pressure to extrude the material, an extruder is always incorporated for pelletisation to take place.

Co-rotating disk extruders

Co-rotating disk extruders consist of two moving, drag-inducing surfaces. The material is conveyed by the action of the two walls and the side of the disks, which forms a wedge-shaped chamber (Tadmor, 1970).

CHAPTER 5 CHARACTERISATION TECHNIQUES

Fillers, additives, resin, paraffin and microcrystalline waxes are the ingredients used to process wax moulding compounds. This chapter describes the basic techniques used to characterise the mechanical, thermal and chemical properties of investment casting filled wax moulding compounds for quality control and to meet specific requirements for investment casting (Aibarro *et al.*, 2001).

5.1 Mechanical properties

The mechanical properties of a pattern are crucial in that a hard, brittle wax pattern may be damaged during the assembly and storage stages in the investment casting process. A wax that is too flexible and soft also may not retain its shape during shelling process. Therefore, three-point bending and impact tests are used to characterise the mechanical properties of wax to avoid the above-mentioned problems.

5.1.1 Three-point bending test

This method is used to characterise brittle materials where tensile, compression and hardness testing are problematical, e.g. very low deformation before fracture occurs. The results of the testing method are sensitive to specimen and loading geometry and strain rate. The parameters of interest are the bending stress and the maximum deflection of a beam. The modulus of elasticity and the modulus of rupture can be calculated. Figure 13 below shows the three-point bending test set-up.

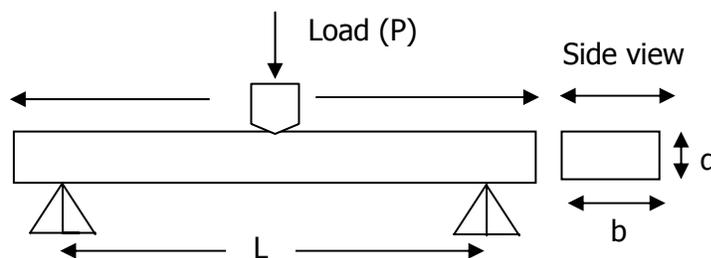


Figure 13: Three-point bending test set-up (ASTM D790, 1983)

Where P is the load, L is the support span, b is width of test beam and d is the depth of tested beam

The stress, strain, modulus of rupture and Young's modulus of bending are calculated using the following equations.

(i) Stress:
$$\sigma = \frac{3PL}{2bd^2} \quad (7)$$

(ii) Strain:
$$\varepsilon = \frac{6Dd}{L^2} \quad (8)$$

(iii) Modulus of elasticity:
$$E_B = \frac{L^3 m}{4bd^3} \quad (9)$$

Where σ_{is} stress, ε is strain, E_b is the modulus of elasticity in bending and m is the slope of the tangent to the initial straight-line portion of the load deflection curve

5.1.2 Impact testing

Impact testing is used to quantify the fracture behaviour of materials. The mechanical tests determine the ability of a material or object to withstand a high loading rate assault. Critical parameters include the fracture energy and the fracture stress. There are basically two types of impact test. Projectile methods include the drop weight test and pendulum tests include the Charpy, Izod and tensile impact test procedures (Callister, 2003).

Drop weight impact test

This method involves dropping a weight on top of a sample from varying heights. The impact energy is calculated from the mass and the drop height, i.e. potential energy. The test result depends on the nature of the damage that the specimen suffers. It can either survive, or be slightly or completely destroyed. In industrial practice, it is common to consider the results obtained from this test as either a fail or a pass at a prescribed drop height for well-defined sample and projectile geometries (ASM Handbook, 2000). In effect this is a quality control technique that is dependent on operator interpretation of the damage.

Advantages of the drop impact test

- Appropriate to moulded samples
- Failure can be expressed in terms of deformation, complete fracture or crack initiation.
- Samples do not have to shatter to be considered to have failed.

Disadvantages of the drop impact test

- Time and resource-consuming, requiring from 50 - 100 samples
- Changing the drop height causes a change in the impact velocity; this exposes a material to different strain rates.
- Causes safety and health hazards as operators need to continuously lift and drop heavy weights.
- Subject to differences in individual assessment of damage (i.e. one person a different opinion to another)

Charpy and Izod pendulum impact tests

A pendulum consists of a single arm and a striking rod, the geometry of which is dependent on the test method to be used. The drop height and mass determine the potential energy. Extra weight can be added to each pendulum unit. The Charpy and Izod impact tests are similar but differ in the ways in which the samples are prepared, notched and clamped, and in the units of measurement.

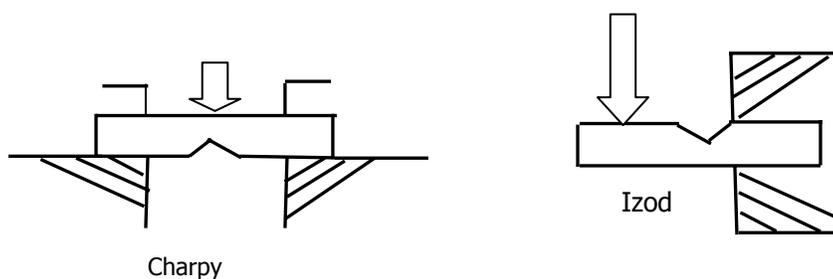


Figure 14: Charpy and impact test set up (Robert, 1985)

In notched Izod testing, the notch faces the pendulum after being mounted in a vice fixture. In Charpy testing, the sample is laid horizontally on two supports against an anvil. The sample is notched in the middle and faces away from the pendulum. This is shown in Figure 14. As the

sample breaks, the energy absorbed is calculated from the height that the pendulum has attained after breakage (Robert, 1985).

Disadvantages of the Charpy and Izod pendulum impact tests

Charpy and Izod pendulum impact tests do not provide information on what happens during impact. Furthermore, the sample can fail internally but display no damage externally (ASTM Handbook, 2000).

5.2 Dynamic mechanical analysis properties

Dynamic mechanical analysis (DMA) analyses a polymeric material's response when an oscillating force is applied to a sample. It basically determines the elastic modulus (or storage modulus, G), the viscous modulus (or loss modulus) and the damping coefficient as a function of temperature, frequency or time. From DMA, the transition regions, such as the glass transition temperature, rubbery plateau and the melting temperature, are identified. DMA is used for product and quality development in the plastics industry (Menard, 2003).

Polymers are viscoelastic materials since they exhibit both elastic behaviour just like a spring when stretched quickly returns to their original state and viscous (dashpot-like) behaviour which resist shear flow and strain linearly with time when a stress is applied. Consider the application of a sinusoidal oscillating deformation to a polymer sample the stress yields:

$$\sigma = \sigma_0 \sin(\omega t) \quad (10)$$

Where σ is the stress at given time, σ_0 is the maximum stress and ω is the frequency of oscillation.

The sample will experience a sinusoidally varying stress in the linear viscoelastic regime. Both the viscous (flow-like deformations) and elastic behaviour patterns of the material affect the resulting stress wave. Taking the derivative of equation (10) gives the rate of stress variation:

$$d\sigma/dt = \sigma_0 \omega \cos(\omega t) \quad (11)$$

Two limiting behaviours are shown by viscoelastic materials: They are represented by the perfect elastic solid and the viscous liquid. These systems are generally pictured as a Hookean spring and a dashpot respectively. The stress and strain for a Hookean spring will be in phase and the response can therefore be written as:

$$\varepsilon = E \sigma_0 \sin(\omega t) = \varepsilon_0 \sin(\omega t) \quad (12)$$

Where ε the strain at is given time, and ε_0 is the maximum stress

This curve is shown in Figure 15. It has a phase lag of value 0° and this represents the in-phase portion of the curve.

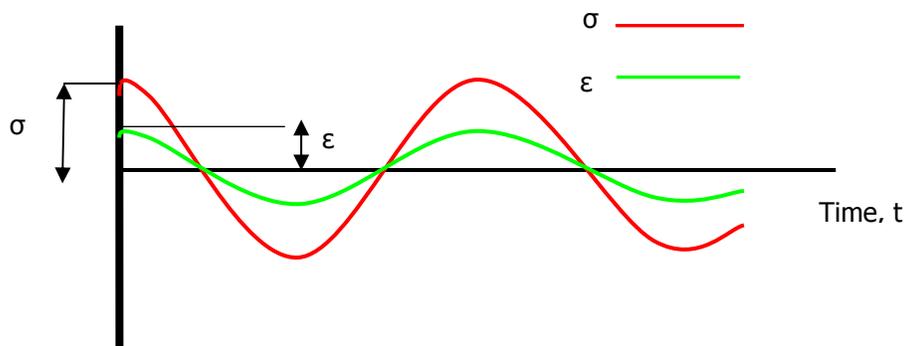


Figure 15: Perfectly elastic solid with no phase lag (Menard, 2003)

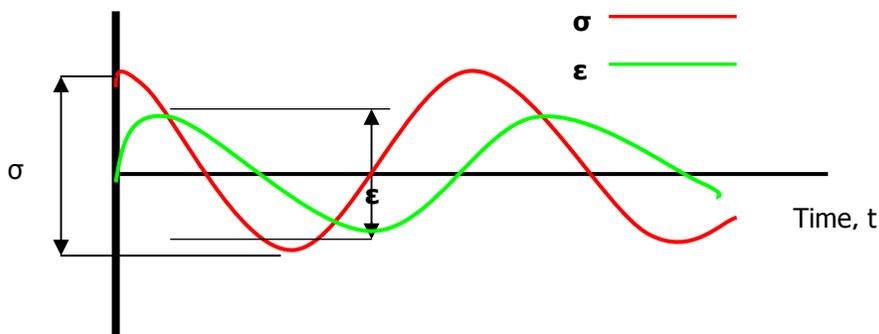


Figure 16: Purely viscous modulus at a phase angle of exactly 90° (Menard, 2003)

According to Newton's viscosity law, the stress in a pure viscous liquid is directly proportional to the strain rate, i.e. the first derivative of strain. Using a dashpot, the various responses in terms of strain rate can then be expressed as

$$\varepsilon(t) = \eta d\sigma_0/dt = \eta \sigma_0 \omega \cos(\omega t) \quad (13)$$

This can further be rewritten as

$$\varepsilon(t) = \sigma_0 \omega \varepsilon \cos(\omega t) = \varepsilon_0 \omega \sin(\omega t + \pi/2) \quad (14)$$

This curve is shown in Figure 16. The phase lag is exactly 90°.

A viscoelastic material exhibits behaviour intermediate between the viscous and elastic limits. There is a difference between the resultant strain and the applied strain at some angles. The elastic response at any time must be added by a phase angle δ ; this can be written as:

$$\varepsilon = \varepsilon_0 \sin(\omega t + \delta) \quad (15)$$

Applying trigonometry, the equation can be rewritten as

$$\varepsilon = \varepsilon_0 [\sin(\omega t) \cos(\delta) + \sin(\delta) \cos(\omega t)] \quad (16)$$

The above equation can be broken into an "in" phase and an "out" phase strain, which is depicted in Figure 17 below.

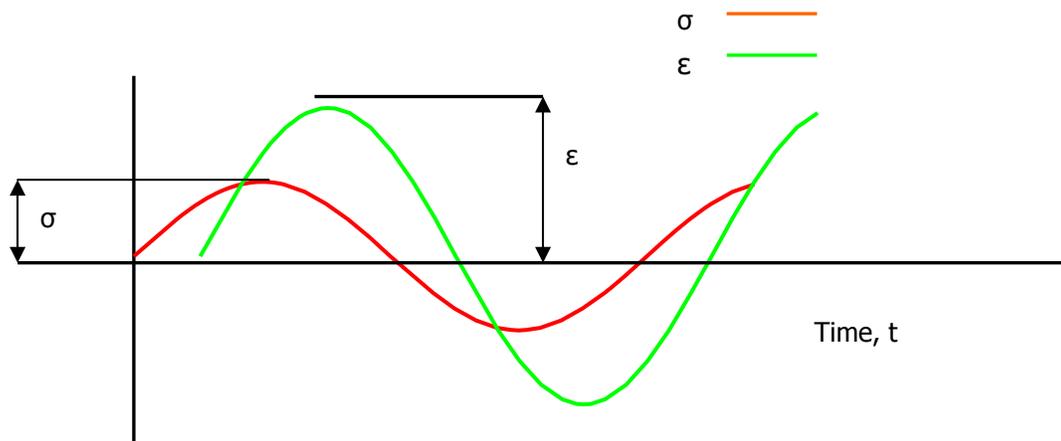


Figure 17: Viscoelastic materials (Menard, 2003)

The vector sum of these two components gives the complex strain of the sample:

$$\varepsilon^* = \varepsilon' + i \varepsilon'' \quad (17)$$

Once all the basic properties are known, all the other properties can be calculated from them.

Table 8 shows the calculation of the remaining properties by DMA.

Table 8: Calculation of material properties by DMA (Menard, 2003)

Property	Formula
Strain	$\varepsilon = \varepsilon_0 e^{i\omega t}$
Stress	$\sigma = \sigma_0 e^{i(\omega t + \delta)}$
Damping	$\tan \delta = \frac{E''}{E'} = \frac{\sin(\delta)}{\cos(\delta)}$
Complex modulus	$E^* = E' + iE''$ $ E^* = \sqrt{E'^2 + E''^2}$
Complex shear modulus	$G^* = \frac{E^*}{2(1+\nu)}$
Complex viscosity	$\eta^* = \frac{3G^*}{\omega} = \eta'' + i\eta'$
Complex compliance	$J^* = \frac{1}{G^*}$
Work stored	$\frac{\varepsilon_0 \sigma_0 \cos \delta}{2}$

Where σ_0 is the maximum stress, ω is the frequency of oscillation, ε_0 is the maximum stress, E' is the storage modulus, E'' is the loss modulus and δ is the phase angle.

5.3 Thermomechanical analysis properties

5.3.1 Therm dilatometry

Most, if not all materials, including investment casting waxes, expand with increasing temperature. Larger volumetric changes are observed during phase changes. Such effects can be problematic with respect to pattern materials as it could cause the mould shell to crack.

Thermal expansion and volume changes are measured using dilatometers. In a typical set-up, a sample is heated at a constant-temperature scan rate in an oven and the dimensional changes are monitored via the displacement of a probe in contact with the sample. The coefficient of linear thermal expansion is defined by:

$$\alpha = \frac{1}{L} \frac{dL}{dT} \quad (18)$$

Where L is a measured length dimension and T is the temperature.

5.3.2 Volumetric expansion

This methodology determines over a range of temperatures the volumetric expansion characteristics of wax patterns. Commercial instruments are available that can generate profiles of volume versus temperature (Monk, 2001).

5.4 Physical properties of waxes

Waxes are classified as “soft” or “hard” depending on whether they can be worked by hand or whether a tool is required. “Hard” waxes are preferred for patterns because soft waxes will deform more easily.

5.4.1 Melting/softening point

Many waxes are highly crystalline and their melting points can be used to distinguish them. In industry there is an additional connotation associated with “melting”, i.e. the temperature at

which the wax becomes sufficiently fluid to be processed. These “melting points” of wax patterns can be determined by using either the ring-and-ball softening point or the Ubelhode drop melt point.

Ring-and-ball softening point. In this method the wax is placed in a water bath and a ball-bearing is placed on top of it. The temperature of the wax is increased until the wax softens enough to let the bearing penetrate through it.

Drop melt point. In this method the wax is placed in a special cup with a small opening and the temperature of the wax is raised until the first drop falls. The softening point indicates the temperature at which the wax changes from solid to liquid. It basically describes the temperature at which the wax is dewaxed during the investment casting process (Monk, 2001).

Congealing point. This is the temperature at which the waxes will not flow under gravity. Softer waxes will flow easily, while harder waxes tend not to bend or deform – hence there are more dimensionally consistent. To avoid pattern deformation, it is advisable that wax should be injected at a temperature 4 - 5°C below the congealing point.

5.4.2 Dimensional analysis

This is used to determine the dimensional stability of wax patterns after injection moulding. Wax is injected into a tool of given dimensions; the wax is cooled at a given controlled temperature. A calliper is then used to measure the length and thickness and this is compared with the tool dimensions and tolerance specification (Monk, 2001).

5.4.3 Density

Density measurement is important in investment casting moulding compounds in that a high density allows fillers to be separated easily from the base wax, to allow the base wax to be reclaimed and reused. It also gives an indication of the degree of mixing achieved.

Actual density can be measured using the Archimedean Principle (Spieweck and Bettin, 1992). This principle states that a solid body immersed in a liquid loses as much of its own weight as the volume of the liquid it has displaced.

$$\rho_s = \frac{A}{A - B} \rho_L \quad (19)$$

Where A is the weight of the sample in air, B is the weight of the sample immersed in water, ρ_s is the density of the sample and ρ_L is density of liquid. The theoretical densities (ρ_c) of the blend were determined using the mixing rule for non-interacting components:

$$\rho_c = \left(\sum_{i=1}^n \frac{w_i}{\rho_i} \right)^{-1} \quad (20)$$

Where ρ_i is density of the component and w_i is the weight fraction of component.

5.5 Thermal properties

5.5.1 Differential scanning calorimeter (DSC)

A DSC design consists of a heat flow path, two pans of which one contains the polymer and one is left empty to act as a reference. These two components are connected to a computer. Using the DSC, the heat capacity can be determined by plotting the difference in heat flow against temperature. The heat flow is heat supplied per unit of time, and the heating rate is the temperature change per unit of time

The heat flow divided by the heating rate gives the heat capacity:

$$C_p = \left(\frac{dq}{dt} \right) / \left(\frac{dT}{dt} \right) \quad (21)$$

Where q is the heat supplied, t is the time and T is the temperature.

DSC can detect the glass transition of a crystalline polymer. When heat is absorbed, the polymer undergoes a glass transition – indicated by a change in its heat capacity. This is depicted in Figure 18.

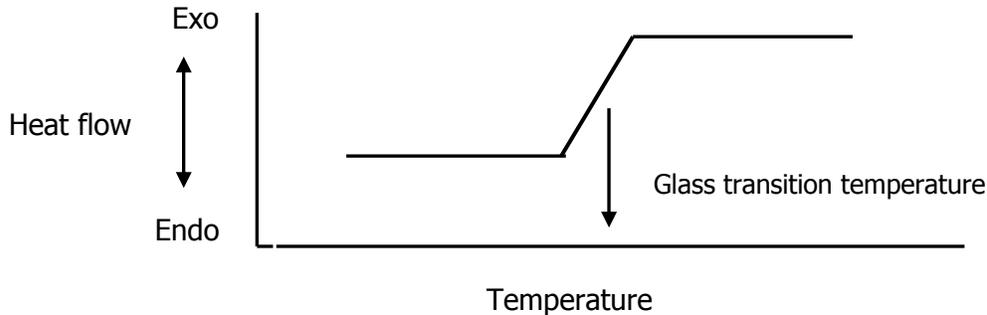


Figure 18: Heat flow against temperature showing glass transition

Above the T_g , the mobility of the polymer chain increases. Above a certain temperature, the chain gains enough energy to form very orderly, refined arrangements called crystals. The formation of crystals gives off heat. Figure 19 shows a plot of heat flow against temperature, with a pronounced peak.

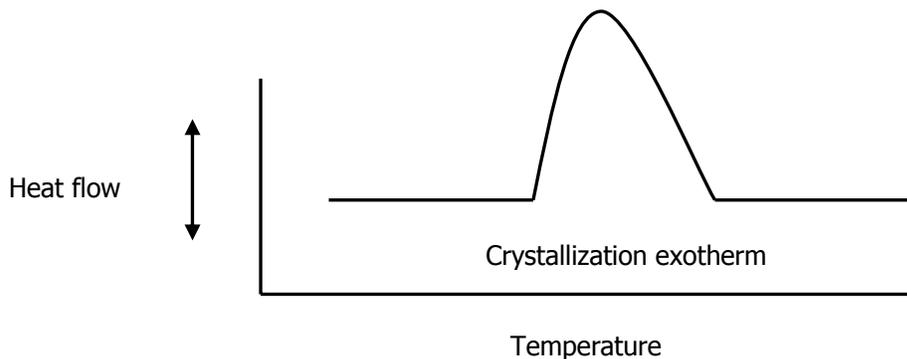


Figure 19: Heat flow against temperature showing crystallisation temperature

The temperature at the highest peak is the crystallisation temperature (T_C). The latent energy of crystallisation can be calculated from the area under the peak. As more heat is added above T_C , the polymer melts and its crystals begin to fall apart. The chains are in disordered arrangement and move around freely. This is shown in Figure 20 below.

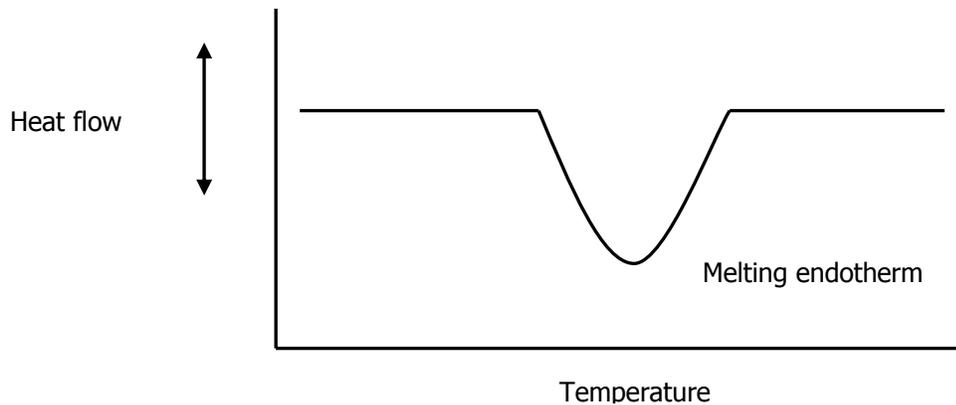


Figure 20: Heat flow against temperature showing melting temperature

DSC can be used to calculate the % crystallinity of a polymer using the heat of melting. The heat of melting can be determined from the area under the melting peak.

$$Area = \frac{heat \times Temperature}{time \times mass} = \frac{JK}{sg} \quad (22)$$

Where the units are such as joules x Kelvins x (seconds)⁻¹ x (grams)⁻¹:

If the area is divided by the heating rate it is then possible to predict the heat given off when a polymer melts.

$$\frac{Area}{Heating \ rate} = \frac{\frac{JK}{sg}}{\frac{K}{s}} = \frac{J}{g} = H_m \quad (23)$$

The energy in joules can be determined by multiplying it by the mass of the known polymer. The heat given off by the part of the polymer sample that was already in the crystalline state before it was heated above T_c equals the total heat given off during melting, minus the heat of crystallisation (Dean, 1995):

$$H' = H_m - H_c \quad (24)$$

5.5.2 Thermogravimetric analysis

The ash content of a wax pattern may be important. This is because an ash content of more than 3% can cause mould reaction during investing process and poor surface finish. Thermogravimetric analysis (TGA) is used to measure the change in mass of a sample against temperature and time. TGA further provides information about the thermal stability of a chemical and its composition. In wax patterns, this measurement includes oxidative stability, decomposition kinetics, moisture and volatile contents, and shelf-life studies using kinetics.

5.6 Rheometry and melt flow index

Viscosity (η) is a measure of the resistance to any deformation. When a shear stress is applied to a solid body, the body deforms until the deformation results in an opposing force to balance that applied, resulting in equilibrium. Even among fluids (i.e. substances that are accepted as fluids), there can be wide differences in behaviour under stress. The value of the viscosity is constant for fluids obeying Newton's law. Such fluids are known as Newtonian fluids. If η is constant, the shear stress is linearly dependent on the velocity slope. This is accurate for most common fluids.

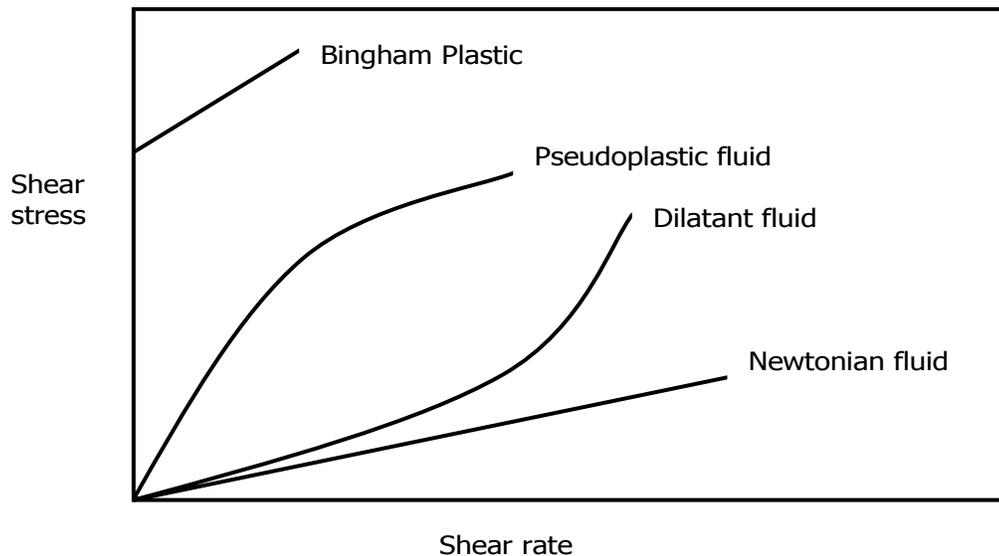


Figure 21: Shear stress vs. rate of shear strain of fluids

For non-Newtonian fluids the value of the viscosity is not constant. There are several examples of these, and they are outlined briefly below.

These categories are based on the relationship between shear stress and the velocity slope (rate of shear strain) in the fluid. These relationships can be seen in Figure 21 above for several categories.

Each of these lines can be represented by the equation:

$$\tau = A + B\dot{\gamma}^n \quad (25)$$

where A , B and n are constants. For Newtonian fluids $A = 0$, $B = \eta$, $n = 1$ and $\dot{\gamma}$ is the shear rate.

Below are brief descriptions of the physical properties of the several categories:

- *Plastic*: Shear stress must reach a certain minimum before flow starts.
- *Bingham plastic*: These fluids do not flow unless the stress applied exceeds the "yield stress". Typical examples include sewage sludge, tomato paste and toothpaste.
- *Pseudo-plastic*: These fluids exhibit a decrease in viscosity with increasing shear rate and hence are often referred to as "shear-thinning fluids". Typical examples include polymer melts, polymer solutions, blood and filled polymer melts.
- *Dilatant substances*: These fluids show an increase in viscosity with increasing shear rate and are "shear-thickening fluids". Typical examples consist of wet sand, starch suspension and gum solution.

Rheology is the study of the deformation and flow of matter (Lenk, 1978). It describes the interrelation between force, deformation and time. The term comes from the Greek word *rheos*, meaning "to flow". From a broad perspective, rheology includes almost every aspect and behaviour that deals with the deformation of materials as a result of an applied stress. In other words, it is the study of the internal response of materials to external forces. Rheology can be applied to all materials, from gases to solids, regardless of their type physical state, or the form in which they are used.

Fundamental to rheology are the concepts of material elasticity and viscosity. Materials will respond to an applied force by exhibiting either elastic or viscous behaviour or a combination of both mechanisms. Solids store mechanical energy and are elastic, whereas fluids dissipate energy and are viscous. The combined behaviour is termed *viscoelasticity*. Common to liquids, solids and substances which are viscoelastic is the phenomenon that if a stress is applied to them, they will strain. If solids are elastic, they deform and return to their original shape. Since fluids are not elastic and, hence, are viscous, their deformation is irreversible.

Rheology is used to describe the properties of a wide variety of materials such as investment-casting waxes. Rheometers are used in the industry at various levels of sophistication to provide information for different purposes, such as quality control, product development and process engineering. The measurements obtained are used to obtain correlations between molecular structure and material properties, and between material properties and behaviour in practical situations. This requires sophisticated mathematical treatments using data obtained from simple rheological experiments. Without rheology, nothing in materials and process engineering can function today.

In a rotational viscometer, a polymer melt is sheared between rotating cylinders, cones or plates, under controlled-stress or controlled-rate conditions (Shenoy & Saini, 1984). There are two types of mechanism for measuring viscosity in rotational rheometers, namely controlled-stress and controlled-rate rheometers. In a controlled-stress rheometer, the torque/shear stress is set and the strain rate is determined. In a controlled-rate rheometer, the shear rate is set and the resulting shear stress is measured. The rheometer geometry and the device used to apply a constant torque or rotation speed determines the type of rotational rheometer (Gebhard, 2000). Rheometers are of three basic geometry types, namely the concentric cylinder, the cone and plate, and the parallel plate. These are shown in Figure 22.

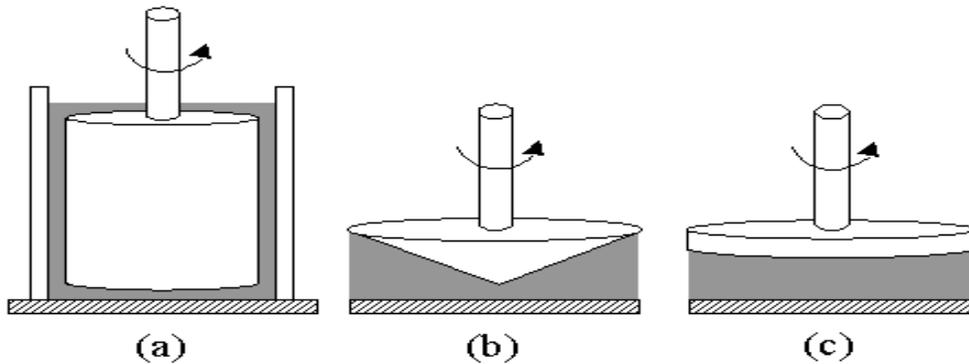


Figure 22: The three types of rheometer geometries: (a) concentric cylinder, (b) cone and plate and (c) parallel plate

For a cone-and-plate rheometer, the shear rate and the shear stresses can be calculated mathematically. The polymer melt is sheared between the cone and the flat plate at a very small angle. Consider a polymer melt or fluid that lies between the plate and the cone with an angle of β , which is normally between 2° and 8° and with a radius R , as shown in Figure 23. Clearly, the speed of the plate and the angle β determine the shear rate (Fenner, 1980).

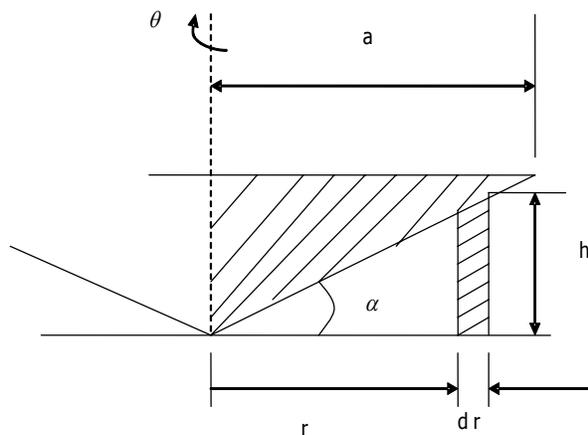


Figure 23: Cross-section of a cone-and-plate rheometer

As the angle is small, the expected flow is shear flow and at steady state condition, the relative velocity between the surfaces is $R \Omega$, where

$$\Omega = \frac{d\theta}{dt} \quad (26)$$

In this expression, θ is the angular displacement of the cone and t is the time.

Hence, the shear rate is given by

$$\dot{\gamma} = \frac{R\Omega}{H} = \frac{R\Omega}{R \tan(\alpha)} = \frac{\Omega}{\tan(\alpha)} \approx \frac{\Omega}{\alpha} \quad (27)$$

Since $\tan(\alpha) = \alpha$ is valid for a small angle, α must be small enough to ensure a shear flow. The shear stress applied is a product of the torque area in the element, $2\pi r dr$, and the distance from the axis of rotation, R . Hence, the total torque applied to the cone is given by:

$$\tau \int_0^a 2\pi r^2 dr = \frac{2}{3} \pi a^3 \tau \quad (28)$$

The torque is equal to the product of the load, W , and the radius of the appliance, b . Therefore, shear stress can be expressed as follows:

$$\tau = \frac{3Wb}{2\pi a^3} \quad (29)$$

The cone-and-plate rheometer has the advantage of being able to measure shear rate and shear stress simultaneously, and therefore can measure both Newtonian and non-Newtonian fluids. Rotational methods can also incorporate oscillatory and normal stress tests for characterising the viscoelastic properties of samples (Kosinski & Caruthers, 1986).

The simple shear flow assumption becomes invalid at high rotational speeds due to secondary flows and instabilities, such as the tendency for cavities to form in the melt near the edge of the cone. Therefore, the reliability of rotational rheometers is restricted.

Rotational rheometers typically operate in the shear rate range 10^{-2} to 5 s^{-1} . In polymer processing practice, much higher shear rates may be found. The applicability of rotational rheometers is therefore limited to characterising materials in the low shear rate range (Fenner, 1985).

Melt flow index

Melt flow indexers are simple capillary viscometers that are used mainly as a quality control technique to characterise the viscosity of polymer melts (Ives, 1971). The conventional technique (ASTM Standard D1238) is as follows: Solid polymer is fed into the hot barrel shown as in Figure 24. When the desired temperature is reached, a fixed weight is placed on top of the piston and the melt is forced out of the die. The mass flow rate of the extrudate is measured and reported in grams per ten minutes.

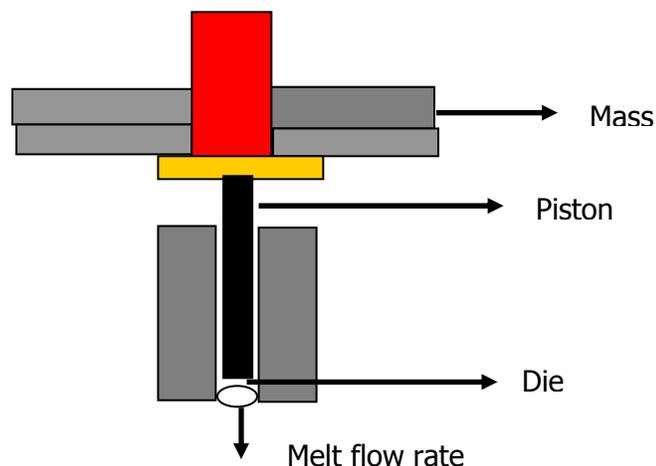


Figure 24: Melt flow indexer

ASTM Standard D1238 prescribes a die diameter of 2,095 mm and a weight of 2,16 kg for polyethylene and polyethylene copolymers such as EVA.

Advantages of the melt flow indexer

- Flow rate measurement is inexpensive and the flow can be measured without difficulty.
- The melt flow index is a standard ASTM measurement.

Disadvantages of the melt flow indexer

- The melt flow index results are not true reflections of viscosity as the capillaries are short and the entrance and exit effects are therefore not negligible.
- Materials may start to degrade chemically before the actual start of the test when they are heated in the barrel for 5 to 10 minutes.
- Inaccurate results are obtained when air is entrapped or if the polymer melt is not fully molten.
- Filler can drop out of the suspension and inaccurate result might be obtained.

5.7 Implications for the development of a urea moulding compound

The prime objective of this study was to develop an alternative to the conventional cooking process for the manufacture of urea moulding compounds. Based on the literature search, it was decided to explore a polymer compounding technique. The main requirement for the new process is increased productivity by reducing the manufacturing time to a minimum while keeping the material cost down by choosing appropriate raw materials and formulations. The material properties were further characterised to check that they do meet the specific requirements of investment casting.

Several screening experiments were done with respect to the raw materials, i.e. the polymer, the wax and the process equipment.

The polymers used were:

- Polyethylene glycol (PEG)
- Polyvinyl alcohol (PVOH)
- Ethylene vinyl acetate (EVA).

PEG was used because it is compatible with PVOH and forms inclusion compounds with urea. Through careful literature research it was concluded that PEG 6000 forms a compatible blend with PVOH only if dissolved in a solution of DMF at a temperature above 70°C. This means that this process in effect returns to the original cooking process, so it was later abandoned.

The concept of eutectics was employed as a possible area of exploration for forming eutectic complex investment casting moulding compounds. Forming a urea-eutectic complex investment-casting compound would reduce the mould temperature and reduce cost.

The following compounds are capable of forming eutectics with urea: benzoic acid and acetamide. The eutectic composition was established by creating different compositions of urea with either benzoic acid or acetamide using a thermocouple apparatus, which determines the melting and crystallisation temperatures.

Process screening experiments were performed to determine the best conventional method to be used to synthesize urea-based investment-casting moulding compounds. A conventional single-screw extruder was used to process a sample containing a mixture of urea, benzoic acid and PEG. However, it was found that it was impossible to compound the mixture since urea degrades just above its melting point to produce CO₂ and NH₃ gas. The experiment was also too dangerous as it could cause an explosion, and it was immediately stopped for safety reasons.

It was then concluded that to synthesise urea-based compounds, the material has to be processed just below its melting point. Thermoplastics such EVA, nylon and PVOH, which have low melting points, were the main possible polymers for use in making urea-based moulding compounds. The main lubricants considered for the work were:

- Stearic acid,
- Paraffin wax,
- Synthetic wax
- Stearic acid soaps

For reasons of cost-effectiveness, EVA was chosen as the possible polymer to be used. Paraffin wax, which is cheap, being manufactured by Sasol South Africa, is also very compatible with EVA and was chosen as the lubricant to be assessed.

A blend of urea prill, paraffin wax and EVA was compounded using a single-screw extruder. From the first trial, the extrudate produced blend-containing prills of urea with EVA. It was also established that a single-screw extruder does not perform dispersive mixing to reduce the prill

to a small size for good mixing. Milled urea was used to ensure more efficient dispersive mixing in the single-screw extruder. However, no success was achieved in compounding the urea-wax-EVA blend. It was then decided to use a co-rotating twin-screw extruder. There was much concern about not damaging the screws of the twin-screw extruder as these are expensive items of equipment and too costly to repair; a twin-screw extruder was therefore rented. It was definitely preferable to use milled urea. The use of a two-roll mill was also considered, since two-roll mills are more economical to use and they offer better dispersive mixing due to elongation flow.

In all the compounding trials, it was possible to compound the urea-EVA-wax blend using either a co-rotating twin-screw extruder or a two-roll mill without any difficulty. However, some of the compounds formed in the trials could not be injection-moulded.

PVOH is an attractive “biodegradable” polymer used in different areas of science and technology, especially in adhesives for paper, wood, textiles, food and pharmaceuticals. However, a polyvinyl alcohol melts and decomposes just above its melting point. Plasticisation technology was applied to lower the melting point of PVOH to allow and improve its processability. Lowering the melting point of PVOH also allows milled urea and other polymer additives with poor thermal stability (low melting points) to be processed with PVOH.

In all the compounding trials, it was possible to compound the urea-PVOH-wax blend using a two-roll mill without any difficulty. However, some compounding trials were not tried using a twin-screw extruder. It was also possible to injection-mould all the urea-PVOH-wax blends without any difficulties.

Based on the many screening experiments done, EVA was chosen as the base polymer to be compared with the PVOH used in the current system. An advantage of EVA is that the plasticisation process is avoided, unlike when using PVOH. A disadvantage of EVA is that, unlike PVOH, it is non-biodegradable and this may therefore have implications for waste disposal. PVOH is also cheaper as it is used in very small amounts compared with EVA.