CHAPTER 1   INTRODUCTION

Metals are essential industrial materials due to their good mechanical properties. Metals combine properties of high strength with the ability to change shape without brittle fracture compared with wood, plastics and stone. This enables metals to be formed into a wide range of shapes. Metals are normally extracted from ores and are prepared using various metal-forming processes such as casting, forging and extrusion. Casting involves the pouring of molten metal into a mould or a die. After cooling, the metal takes the shape of the mould and can then be used to form metal components. Common examples of casting processes include sand, dies, centrifugal casting, full moulds, squeeze, investment casting, etc. Alternatively, forging can be used to form metal components. Forging involves forming a metal by heating it in a forge and beating or hammering it into the required shape.

Investment casting is accepted as the most versatile, flexible process in that it produces "near net-shape" metal components compared with other metal-forming processes. Near net-shape provides metal components that are accurate in dimension and surface structure and thus this reduces the amount of waste material in metal casting produced during finishing step compared with other types of metal forming process.

The investment casting process normally involves a disposable wax pattern by injecting wax into a metal die, building a ceramic shell mould by dipping the wax pattern into a slurry, dewaxing the mould and casting the molten metal into the resultant cavity.

Traditionally, urea-based investment casting moulding compounds are synthesised using a cooking process. Nowadays, industries use fast processes, such as conventional extrusion processes, to increase the rate of throughput. The commercial cost performance ratio is another important aspect to be considered. Since waxes are expensive and do not have good mechanical properties, effort is being focused on maximising the filler content and concurrently maintaining the following requirements for quality control needed by an investment caster:

- The pattern must not change shape (creep) during storage/handling
- The pattern must not break during the handling, assembly and storage steps.
- The pattern must not react with the refractory mould.
- The pattern must burn out of the refractory mould leaving an ash content of 0,014 wt % or less.

- The pattern must not shrink or distort in order to produce accurate dimensional stability close to the accepted tolerance.
- It must be possible to produce the pattern at minimal lead times using conventional extrusion methods.
- It must be possible to produce the pattern cost-effectively.
- The pattern must not emit carcinogenic material in order to be environmentally friendly.
- The pattern should have a good surface finish.

Urea is a highly crystalline organic compound commercially available in prill form. It is inexpensive but it degrades just above its melting point of ca. 134°C to produce ammonia and carbon dioxide and therefore cannot be processed using conventional extrusion processes.

Polyvinyl alcohol (PVOH) is an attractive biodegradable polymer used in different areas of science and technology, especially in adhesives for paper, wood, textiles, food and pharmaceuticals. It offers flexibility, transparency and toughness compared with other barrier polymers. However, the melting point of the crystallites of PVOH is above the thermal degradation temperature which is ca. 170°C. For this reason plasticisation technology using glycerol is employed to lower the melting point of polyvinyl alcohol to just below the melting point of urea. This improves the processability of both urea and PVOH, and also eliminates the required slow cooking process if the conventional extrusion process is employed. However, plasticisation is a time-consuming process and because urea is very soluble in water, it cannot be pelletised directly using water.

The use of a hot-melt adhesive such as ethylene vinyl acetate (EVA) is highly advisable since it offers good adhesion to a variety of materials and it is not expensive. Also, EVA offers a wide range of high-melt flow indices and low melting temperatures. Because of its low melting temperature and its good compatibility with wax, EVA can be compounded with urea below its melting point.

Low cost, high lubricity and low melting viscosity are the main properties that make wax a valuable organic pattern material in investment casting.

The present study considered the following important aspects of urea-based moulding compounds for investment casting:

- The optimisation of the formulation with regard to the content of urea, PVOH, EVA and wax
- The development of novel compounding techniques to be used to synthesise EVA urea-based and PVOH urea-based moulding compounds for investment casting.
- Characterisation of the moulding compounds to meet the requirements of investment casters by comparing them with a characterised industrial cooked urea-based moulding compound.

The study is, however, limited in that urea/PVOH moulding compounds were produced using a two-roll mill only. The use of conventional extrusion processes was not investigated.

CHAPTER 2   INVESTMENT CASTING

2.1   History of investment casting

Investment casting originated several thousand years ago: Ancient Egyptian and Chinese museum pieces suggest that they were made by investment casting processes (Little, 1977). According to Black, *et al.* (1984), "Dentists have also used the process since the turn of the century". It did not, however come into common industrial use until World War II (1939-1945) when high-quality jet turbine blades and supercharger buckets for aircraft engines were in great demand.

2.2   Investment casting process

Figure 1 illustrates the current industrial investment casting process. It starts with the manufacture of a pattern using an injection moulder or a wax injector. The patterns are attached to a common sprue and then invested, i.e. "dipped", in slurry to create a thin coating on the surface. Dipping in a refractory slurry mixture is repeated until a coat of the correct dimension is achieved and finally a granulated refractory 'stucco' shell is applied (Repp, 1994). The pattern-sprue system is then conditioned and left to dry.

The coated cluster is then placed in a boilerclave where the pattern melts (de-waxing) and runs out through the gates, runners and pouring cup. The ceramic shell moulds are fired in a furnace to form the final mould walls. In the process, leftovers of the wax burn out. The hot moulds are filled with molten metal and allowed to cool. After the moulds have cooled, the ceramic material is removed from the casting cluster by either mechanical or chemicals means. Finally, the individual castings are removed, machined and polished. Figure 1 depicts the entire process of investment casting.

Advantages of investment casting
- Precision, flexibility, reliability and good surface finish is there in investment casting compared with other metal-forming processes.
- There is no requirement to make draft angles to give any accuracy or versatility needed.

- The investment casting process is also versatile in that a wide range of materials can be formed and cannot be formed by any other metal forming process.
- Because of the high degree of dimensional accuracy and the excellent surface finish, little or no machining is required, leading to savings on raw material.

Disadvantages of investment casting

- The size of parts is limited because it becomes difficult to form moulds for large objects.
- The machinery and dies are expensive.
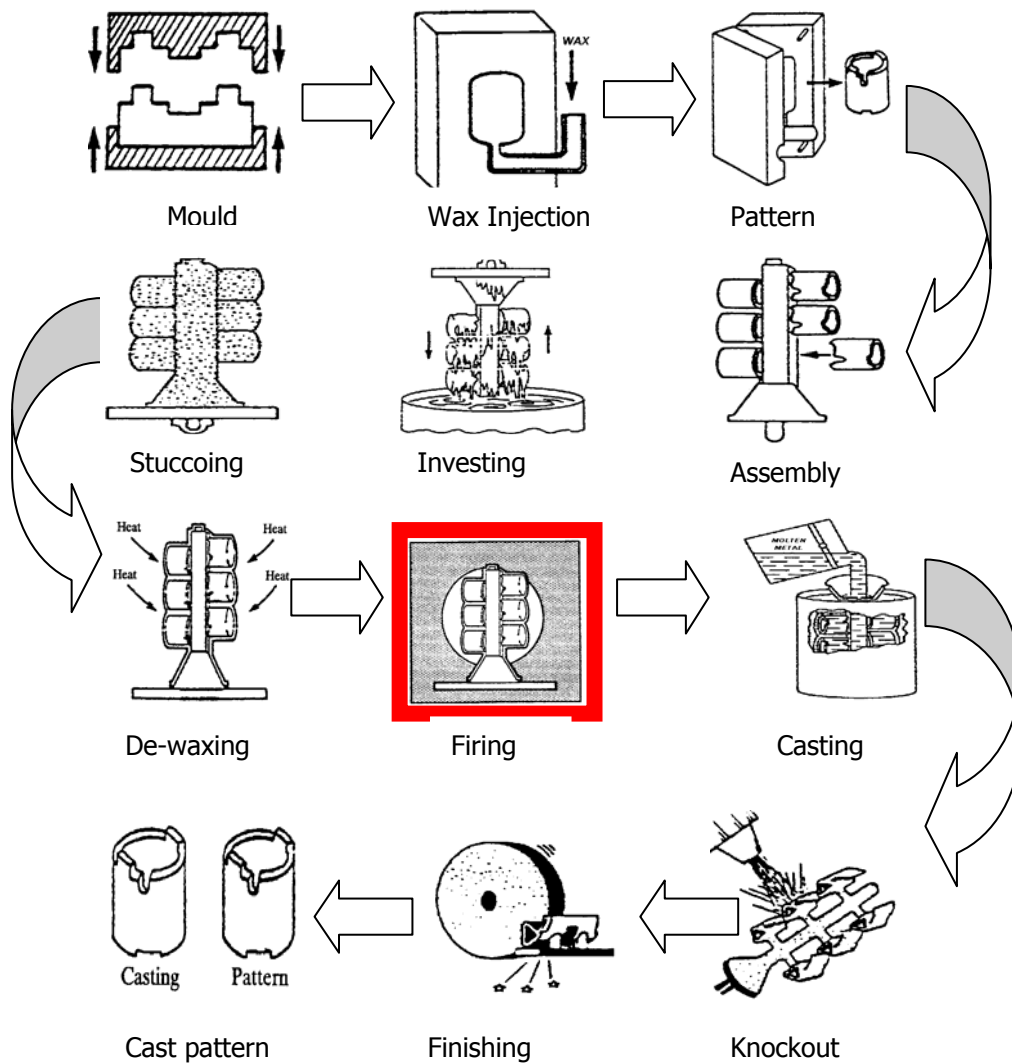- The unit cost is high and the process is labour-intensive.

Figure 1:   Investment casting process (Biam, 2004)

CHAPTER 3   MOULDING COMPOUNDS FOR INVESTMENT CASTING

3.1   Wax based moulding compounds for investment casting

Fillers, additives, resin, paraffin and microcrystalline waxes are typical ingredients used to formulate wax-based moulding compounds for investment casting. There are basically five types of wax based moulding compounds for investment casting, as discussed below (Rajesh, 2004).

1)   Straight or unfilled moulding compound

Straight or unfilled investment casting pattern waxes are waxes that do contain any filler. These waxes can be recycled and reconditioned easily in contrast to other investment casting waxes. Straight patterns are more expensive than filled moulding compounds (Rajesh, 2004). There are mainly used for runners.

2)   Filled moulding compound

Filled patterns contain fillers to extend the primary waxes. The inclusion of low-cost fillers reduces the cost of the compound but, more importantly, they reduce the linear thermal expansion coefficient of waxes. These reduce in surface defects, such as sinks and cavitations.

3)   Emulsified "fillers"

This type of pattern utilises water as a "filler material". Pattern wax containing emulsified water reduces the cost even further as it eliminates the use of solid fillers. Also there are easily removed from ceramic shell in the de-waxing process without cracking of the shell.

4)   Adhesive waxes for the assembly of wax patterns

Adhesive waxes are used to assemble patterns for the main sprues. There are generally of high strength to hold the weight of heavy assemblies.

5)   Patching and repair waxes

These wax moulding compounds are used to repair defects such as flow lines, sink marks and holes due to air entrapment.

3.3 Other moulding compounds for investment casting

1)   Mercury pattern compounds (Mercasting, 2006)

In this case frozen mercury is used as a pattern material instead of wax. Liquid mercury is poured into a mould where it freezes at low temperatures. Then it is removed and coated with cold refractory slurry to the required thickness. The refractory shell is dried at low temperature the shell and mercury are brought to room temperature and the mercury is melted out. Complex parts can be made using mercury. Very close tolerances and excellent surface finish can be obtained but it is a very expensive method.

2)   Ice pattern compounds (Zhang, 1999)

The Rapid Freezing Forming (RIF) is similar to the Melt Extrusion Modelling (MEM). It uses pure water as a pattern material. At low temperature, water is sprayed through a nozzle to a selected place under the computer's precise control, and is freezed rapidly. The solid part is built from the bottom up to the top layer-by-layer. Advantages of using ice patterns include: High precision (because ice pattern shrinks on melting, i.e. it does no expand like wax patterns), low cost and the environmentally friendly nature of water.

3.3 Principles of compound formulation

Fillers, additives, resin, paraffin waxes and microcrystalline waxes are the ingredients used to process wax based investment casting moulding patterns. Examples of wax moulding compounds include:

Polyethylene terephthalate investment casting moulding compounds

Guinn (2002) invented a wax pattern containing up to 50 wt % polyethylene terephthalate (PET) powder. The use of PET as a filler reduces the thermal contraction and expansion properties of wax, increasing the degree of dimensional accuracy. PET is relatively cheap compared with other inert fillers, can be easily removed from the mould without any form of shell cracking, produces extremely low ash when burned and is compatible with fillers such as organic acids, cellulose acetate, urea, bisphenols, polyacylates, polystyrene and other high-melting-point polyols. It also has a higher specific gravity that ranges between 1.31 and 1.45 g/cm^3, which allows it to be separated from the base wax for reclamation. The PET formulation used in the research is shown in Table 1.

Table 1: **Formulation of an investment casting compounding containing polyethylene terephthalate (PET) as filler (Guinn, 2002)**

Compound	Mass %
Paraffin wax	14
Microcrystalline wax	7
Candelilla wax	4
Aliphatic C5 hydrocarbon resin	10
Polyterpene resin	23
Polyethylene resin	2
Polyethylene terephthalate	40

Urea based investment casting moulding compounds

Fujita (1990) synthesised a urea pattern moulding compound based on a PVOH binder together with eutectic formers. The latter ingredient purportedly improves the processability of the

compound by reducing the melting point of urea. Typical formulations contain up to 95% urea. Fujita (1990) claims that urea forms a eutectic mixture with the following substances: benzoic acid, benzene sulphonic chloride, barium salt, benzoyl chloride, glycine, naphthalene and glutaric acid. According to Fujita (1990), good results are obtained when the polymer contains 1 – 8 wt % benzoic acids. The advantage of this invention is that the pattern (compound) can be injection-moulded at very low pressure, minimising tooling cost and producing a pattern with an excellent surface finish and a close dimensional stability.

Urea patterns are easily removed by melting from the ceramic shell moulds. Since urea is water-soluble, it can also be removed using steam. However, the water-solubility implies that urea easily leaches out of a wax formulation as a result of humidity or contact with water from slurries. Another disadvantage is that urea degrades easily and therefore it presents processing problems.

Urea is also used as a filler in wax investment casting patterns (Horton, 1988). It reduces the linear thermal coefficient of expansion and increases the stiffness of wax in investment casting patterns, leading to the accurate dimensional stability of patterns (Guinn, 2002). Urea is water-soluble and can therefore be easily removed from moulds using steam. However, its water solubility and hygroscopic nature increase the chances of urea leaching out of the wax formulation under ambient conditions or by water from slurries.

Sturgis *et al*. (2001) proposed polycarbonate binders (at 10% to about 50% by mass) to reduce the thermal expansion coefficient of wax patterns.

3.4   Fillers

Fillers are solid granular materials that can be dispersed into a polymer matrix, without affecting the molecular structure of the polymer. Fillers are used to improve the mechanical properties of polymers. They are low in cost and can be used at high volume loadings to provide economical compounds (Gächter & Müller, 1984). Table 2 summarises the important properties that make fillers useful in the plastics industry.

Table 2:   Useful properties of fillers in polymers (Gächter & Müller, 1984)

Properties	Advantage
Mechanical and physical	Fillers increase hardness, impact strength and density; they improve surface quality and dimensional stability.
Thermal	Fillers reduce the linear coefficient of thermal expansion and the contraction of compounds.
	Fillers offer high heat-deflection temperature, high resistance to thermal shock, and good flame and glow resistances.
Chemical	Fillers offer good chemical resistance, weather resistance properties, and low water absorption.
Electrical	Generally, they significantly increase the porosity, reduce the dielectric strength, and lower the dielectric constant and dissipation factor.
Tribological	Wear rate is reduced.
Economic cost	Fillers are cheap and therefore offer low cost per unit volume of a material.

Fillers materials are usually inert and act as a bulking agent (Fielder, 1995). Investment casting fillers are either ceramic in nature or are amorphous polymers that feature low coefficients of thermal expansion. Waxes undergo a large volume change when they melt or crystallise. This is highly undesirable when precision moulds are required. Since fillers do not melt, they tend to ameliorate the solidification shrinkage effect of the wax.

Fillers that have been used in pattern waxes include various dicarboxamides and related compounds, isophthalic acid, pentaerythritol, hexamethylenetetramine, urea, terephthalic acid, PET, water, and normal and cross-linked polystyrene or methyl methacrylate. Good fillers in investment casting waxes should:

- Be inert to the base wax and thermally stable.
- Be spherical and have a small particle size to ensure a smooth surface finish.
- Have a minimal ash content to minimise the formation of undesirable material during the dewaxing and firing process.

- Have a specific gravity similar to that of the wax pattern to minimise settlement.
- Have a good surface finish when injection-moulded.
- Be environmentally and user-friendly.
- Be inexpensive.

3.4   Urea

Urea is produced commercially. Because it is highly hygroscopic, it is sold commercially in prill form to avoid caking and for make it easy to handle (Anon, 1993). The main properties that make urea an important organic compound in industrial applications are listed in Table 3.

Table 3:   Crucial properties of urea (Anon, 1993)

Property	Advantages
Chemical	Forms an inclusion compound and eutectics; is fully soluble in water and partially soluble in alcohol.
Thermal	Reduces the linear thermal coefficient of thermal expansion, contraction of compounds and thermal conductivity.
Mechanical	Has good dimensional stability; increases hardness and reduces creep.
Electrical	Increases porosity, reduces the dielectric strength and raises the dialectic constant and dissipation factor.
Economic	Is one of the cheapest fillers in the world
Environmental	Is biodegradable and produces no carcinogenic material.

3.4.1 Applications of urea

Urea ($CO(NH_2)_2$) is mostly used in agriculture as a fertiliser. Statistical data from 29 urea-manufacturing plants in the United States show that 85% of urea was used as fertilisers, 3% in animal feed and the remaining 12% in plastics and in other uses (Anon, 1993).

Pharmaceutical applications

Urea and malonic acid react to form barbituric acid. Urea is also used in the production of various acylureas and urethanes for use as sedatives and hypnotics.

Applications in resins

Melamine is formed by the dehydration of urea. Melamine is used primarily in the production of melamine-formaldehyde resins for laminates, moulding compounds, coatings and textile finishes (Meyer, 1979).

The manufacture of UF resins involves the reaction of formaldehyde with urea under controlled conditions. Adhesives based on formaldehyde are used as binders in the production of reconstituted wood panels, such as particleboard, plywood, medium-density fibreboard, laminated veneer lumber, finger joints and laminated beams. UF resins and other related formaldehyde resins are also used in resin-impregnated decorative paper laminates, fibreglass insulation binders, foundry cores, pulp and paper processing aids, paper sizing, textile treatments, paints and enamels, and miscellaneous joinery applications (Anon, 1993).

Agricultural applications

In fertilisers, urea is used as a nitrogen-releasing agent since it hydrolyses to form $2NH_3$ and CO_2.

3.4.2 Physical and thermal properties of urea

Urea has definite advantages as a primary moulding material. It has a low coefficient of thermal expansion. The volume of the melt is lower than that of the solid near the melting point (Meesen & Petersen, 1986). This facilitates the removal of the pattern from the shell without causing it to crack (see Figure 2). Urea is water soluble and a crystalline solid.
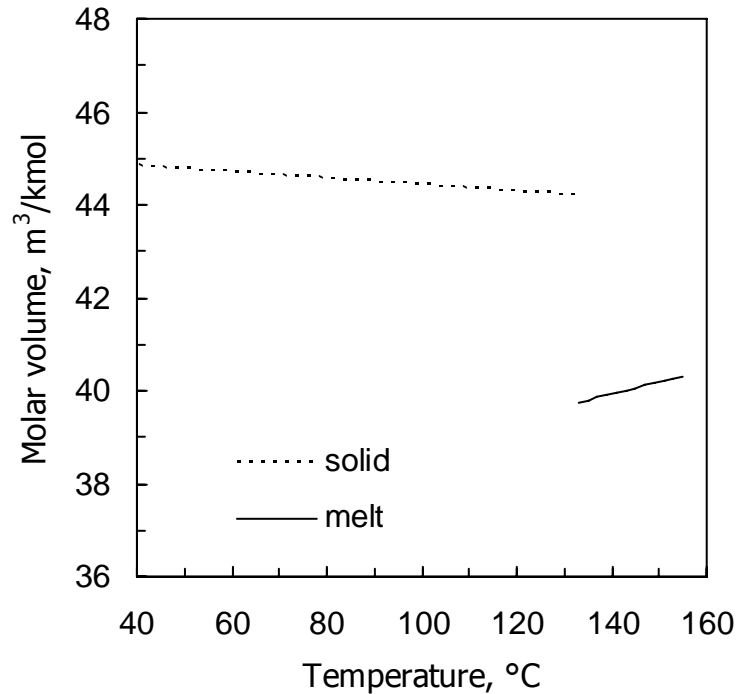
Figure 2: **Molar volume of urea as a function of temperature (adapted from Meesen & Petersen, 1986)**

Urea eutectics (Sekiguchi & Obi, 1961)

Although urea has highly desirable thermo-volumetric properties, it unfortunately starts to decompose at temperatures just above its melting point. Fortunately, the addition of a third component will cause a reduction in the melting point, the so-called "freezing point depression" or "eutectic formation" phenomena. Simple eutectics are based on binary mixtures that have negligible solid–solid solubility but in which the liquids show complete miscibility. Thermodynamically, the solids system is an intimately blended physical mixture of its two crystalline components.

Urea forms eutectic mixtures with methyl urea, dimethyl urea, acetamide, benzoic acid, etc. For example, when urea and acetamide are mixed, heated and cooled at different compositions, a eutectic composition with a minimum freezing point is formed as urea and acetamide crystallise simultaneously (Sekiguchi & Obi, 1961). Figure 3 below depicts the phase diagram of the urea-acetamide system as determined in this study.
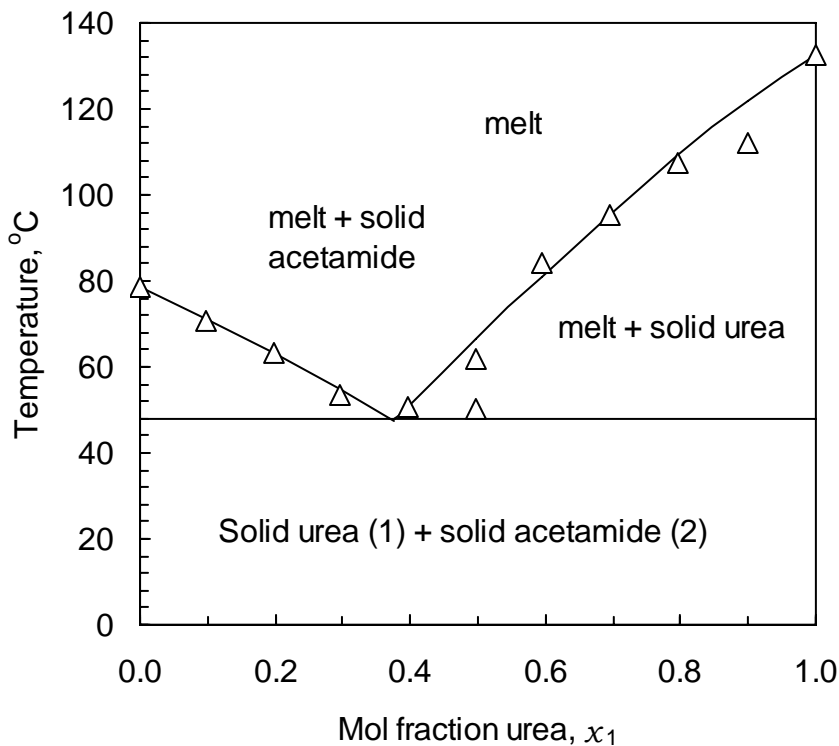
Figure 3: **Phase diagram for the urea (1) – acetamide (2) system (Walbrug, 2006)**

Urea inclusion compounds

Urea forms clathrates, i.e. inclusion compounds with straight-chain hydrocarbons. The urea crystal host structure consists of extensively hydrogen-bonded arrangements of urea molecules. They are arranged such that they form parallel, one-dimensional tunnels. The distance between the centres of adjacent tunnels is ca. 8.2 Å.

The tunnels are filled with a dense packing of guest molecules to make the host structure stable. The diameters of these tunnels are ca. 5.5 – 5.8 Å. The guest molecules must be sufficiently long, with a limited degree of substitution (Sang-Ok & Harris, 1999).

The formation of urea inclusion compounds involves the growing of crystals and a recovery mechanism. A typical preparation procedure for inclusion compounds involving urea (the "host")

and the "guest" is as follows: Both are separately dissolved to form saturated solutions in methanol at 55°C. The combined solution is warmed and continuously stirred. A white precipitate is obtained over the period of a day; it is further filtered and washed with warm toluene (Sang-Ok & Harris, 1999).

3.5   Polymers

Polymers are composed of long molecule carbon and hydrogen based chains. Polymer morphology refers to the structural form (packing) adopted by its collection of molecule chains. Polymers can be classified as being either *amorphous* or in a *semi-crystalline state*. The molecules of completely amorphous polymers exhibit an irregular microstructure.   Crystalline polymers have sufficient molecules to form regular structures (organisation of atoms along the chain).

The molecular motions that do occur in amorphous polymers determine the *glass transition temperature*. These motions include the conversion of entire molecules, "wriggling" and "jumping" of segments of molecules, the movement of atoms in the main chain or in side-groups on the main chain, and the vibration of atoms about the region of equilibrium (Rodriquez, 1989).

The glass transition temperature (T_g) is the temperature at which the polymer begins to exhibit long-range, co-operative segmental motion. Below T_g, amorphous polymer chains are effectively frozen and cannot flow under applied stress; the type of motion is also restricted to vibration modes. Thus the material is hard and glassy. Above T_g, there is enough thermal energy for the chains, through co-operative rotation, to flow under applied stress. The company of large-scale segmental motion above T_g produces an increase in the free volume. *Free volume* is the difference between the actual and occupied volumes of a polymer (Sperling, 1992). The free volume can be described as the "space" that is available to polymer chains. An increase in the free volume of a polymer results to an increase in the "space". This provides more mobility and thus produces a less rigid and more flexible polymer. A graph of polymer free volume vs. temperature is shown in Figure 4. The graph shows that the free volume is constant below T_g

but increases with temperature above T_g. For all polymers, the ratio of free volume to total volume is about 0.05 at T_g.
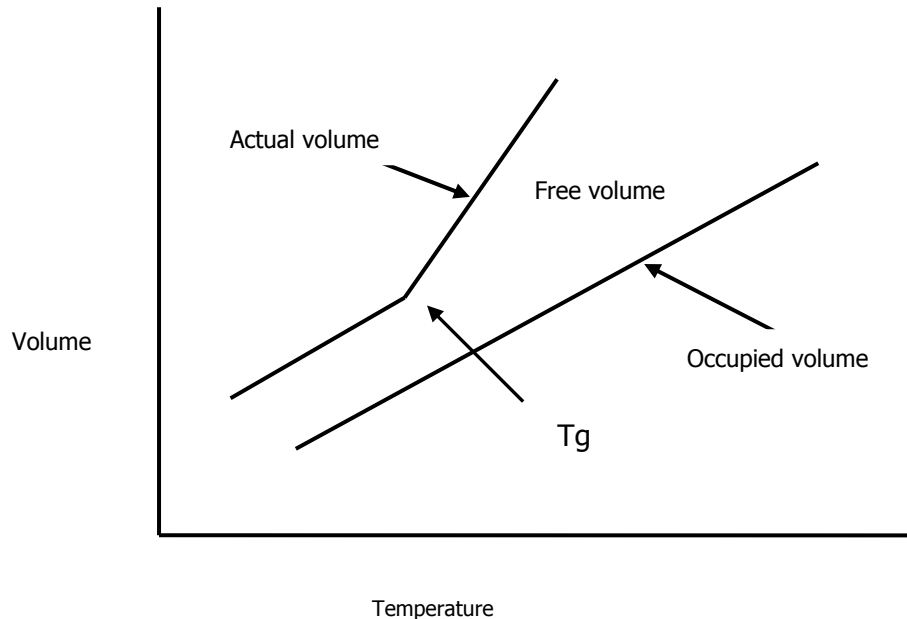

Figure 4:   Polymer volume versus temperature (Sperling, 1992)

Polymers offer flexibility, high resistance to rupture and excellent adhesion to a wide range of substrates. The most common types of resins used in investment casting include polyethylene, ethyl cellulose, nylon, polyvinyl alcohol, ethylene vinyl acetate and vinyl acrylate (Horton, 1988).

3.5.1 Ethylene vinyl acetate

Ethylene vinyl acetate (EVA) is a copolymer of ethylene and vinyl acetate. The vinyl acetate groups are distributed randomly along the long polymer chains (Elvax, 2004). Different EVA grades are distinguished on the basis of their vinyl acetate (VA) content and their melt flow index (MFI). The latter property relates back to the molar mass of the polymer. The physical and mechanical properties of selected EVA grades are shown in Table A4 in Appendix A.

EVA copolymers are commercially available at VA contents ranging from 18 - 40% VA and 0.4 - 500 MFI. EVA polymers are applied in adhesives, sealants, wax bends, hoses and tubing, wire and cable insulation. EVA is the third major class of hot-melt adhesives used in industrial applications (Elvax, 2004).

Physical and chemical properties of EVA

EVA resins soften gradually and continuously with increasing temperature and do not exhibit much solid-to-liquid expansion during heating or contraction during cooling. In summary, resins are used to offer the following important properties (Elvax, 2004):

- Flexibility
- High cohesive strength and compatibility
- Excellent adhesion to a wide range of substrates
- High resistance to rupture
- Lower coefficient of thermal expansion.

Compatibility of EVA and paraffin wax

EVA resin is compatible with wax because it also contains long sequences of $-CH_2-$ units that are linked together. If its crystallisation temperatures overlap with that of the wax, co-crystallisation occurs, with these sequences being incorporated into the wax crystals. This co-crystallisation process allows the EVA resin to reinforce the wax, making a compatible blend. Such blends show significant improvements with respect to mechanical properties such as toughness. EVA resins with 18 to 28 wt % vinyl acetate content melt at 70 - 87°C and freeze at 66°C. This range overlaps with that for paraffin waxes. This is the reason why the paraffin waxes were chosen as candidate lubricants in this study.

At VA content levels greater than 28 wt %, EVA and wax become less compatible due to changes in the freezing point but also because there will be fewer long $-CH_2-$ sequences. Vinyl acetate sequences are not incorporated into wax crystals.

Figure 5 shows the compatibility relationship between vinyl acetate content and wax using the cloud and freezing point. Cloud point is the temperature where the first crystallites start to

form. The cloud and freezing point were measured for blends of 10% EVA and paraffin wax at different VA contents, using a differential scanning calorimeter (Elvax, 2004)
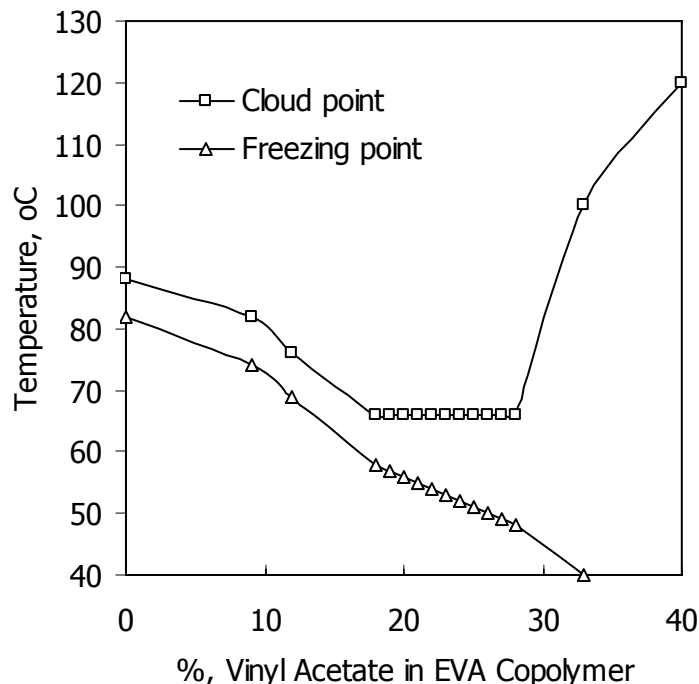

Figure 5: **Cloud and freezing point for 10% EVA, with different VA contents, dissolved in paraffin wax (Elvax, 2004)**

3.5.2 Polyvinyl alcohol

Polyvinyl alcohol (PVOH) is a water-soluble resin produced by hydrolysing polyvinyl acetate. PVOH products are divided into two main groups, namely full hydrolysed and partially hydrolysed. The two groups differ in their physical properties, as shown Table A2 in Appendix A. Commercially, PVOH is available in the form of white granules. The properties that make PVOH useful in industrial applications are given Table 4.

PVOH offers a combination of excellent film-forming and bonding characteristics. This makes it useful in a variety of applications. Examples of PVOH adhesives applications include: paper and paperboard sizing and coating, textiles, building products and ceramic processing.

The melting point of PVOH is above the thermal degradation temperature. Therefore PVOH has to be plasticised to improve its processability.

Table 4:   Physical properties of polyvinyl alcohol (Finch, 1992)

Property	Advantages
Chemical	Chemically soluble in hot water, but insoluble in cold water.
Permeability	High degree of impermeability to gases; forms a coating that provides excellent barrier properties.
Mechanical	High tensile strength; forms a tough, abrasion and tear-resistant film if plasticised. Good adhesive properties.
Optical	Practically opaque.
Moulding	Can be extruded and compression-moulded if plasticised.
Oil and solvent resistance	Resistant to animal and vegetable oils, greases and petroleum hydrocarbons.
Other	Biodegradable, environmentally friendly.

3.6   Plasticisers

A plasticiser is a material of low molecular weight added to polymeric materials such as paints, plastics or adhesives to improve their flexibility and lower their glass transition temperature (T_g). Plasticisers interact with polymer chains on the molecular level to increase chain mobility and to speed up the viscoelastic response (George, 2004).

Plasticisers are commonly classified according to the chemical family to which they belong. Polyvinyl chloride (PVC) is the polymer most often plasticised. PVC plasticisers include esters, phthalates and chlorinated paraffin.

3.6.1 Glycerol

Glycerol is a good plasticiser for polyhydric polymers such as PVOH. Glycerol is an alcohol with a three-hydroxyl group in its chemical structure. It is a clear water-white, hygroscopic, colourless,

odourless, non-toxic and non-irritant liquid (George, 2004). The physical and chemical properties of glycerol are listed in Table A5 in Appendix A.

Glycerol is obtained from glycerides during the process of soap manufacture and fatty acid production. Fat is reacted with caustic soda solution to form soap and glycerol. Glycerol is available in liquid form and should be stored in waterproof containers due to its hygroscopicity.

Glycerol and its esters are used mainly in cosmetics and toiletries, pharmaceuticals, food and beverages, industrial plasticisation of polymers, etc. The beneficial properties that make glycerol useful in industrial applications are given in Table 5.

Table 5:   **Industrial beneficial properties of glycerol (George, 2004)**

Property	Advantages
Rheological	Modifies the flow properties of polymers.
Mechanical	Improves ductility and improves impact resistance.
	Increases elongation and lowers the tensile strength.
Optical	Improves optical clarity.
Processability	Lowers fusion, gelation and melting temperature, and this improves material processing ability (lowers the degradation rate).
Permeability	Improves gas permeability.
Biological attack	Increases biodegradability attack.
Compatibility	Improves compatibility between polymers with additives.
Solubility	Completely soluble in water and alcohol; insoluble in hydrocarbons.

3.6.2 Mechanism of plasticisation

The first theory of plasticisation was developed between 1930 and 1940 (George, 2004). There are two classical theories explaining the plasticisation of polymers, namely the *gel theory* and the *lubricity theory* (Kirkpatrick, 1940). The free volume theory was developed later between 1948 and 1958.

Lubricity theory (Kirkpatrick and Houwink, 1940)

Kirkpatrick and Houwink (1940) developed the lubricity theory of plasticisation. The lubricity theory states that the role of a plasticiser is to reduce the intermolecular friction between polymer molecules, so that the molecules can slip and slide over each other.

The gel theory (Aiken, 1947)

The gel theory supposes that the polymer structure forms a three-dimensional "honeycomb" structure. It states that the polymer's rigidity can be attributed to this three-dimensional network. The plasticiser reduces the polymer-polymer union and thus reduces the rigidity of the polymers. There is a dynamic equilibrium involving solvation-desolvation of the polymer by the plasticiser and aggregation-desegregation of the polymer chains themselves. Thus the success of the plasticiser depends on the strength of attraction involved and on the mobility of plasticiser's molecules.

Free volume theory (Fox and Flory, 1948; Ueberreiter and Kanig, 1952)

After the lubricity and gel theories, the free volume theory emerged from the evolution of different properties of polymers as a function of temperature, specific volume, coefficient of thermal expansion or viscosity. This theory, postulated by Fox and Flory, further explains some properties of plasticised polymers. According to Fox *et al*. (1948), the viscosity at any glass transition temperature is approximately 10^{12} Pa.s, independent of the polymer's chemical structure. The free volume theory considers the available space or "free volume" between the molecules. At high temperatures this free volume is large. Fox and Flory defined the free volume at temperatures above the glass transition temperature. The free volume at all temperatures should be zero for all kinds of glasses. Kanig suggested that free volume is the difference between the volume measured for the crystals and the volume observed at zero temperature, glass or liquid, for a given use (Ueberreiter, 1952).

It is not easy to measure specific volume at absolute zero temperature and therefore this makes the theory behind free volume somewhat vague. Above T_g the segments are so densely packed that internal mobility is negligible.

Some models were developed to correlate the free volume fraction with T_g for polymers. These are discussed below.

Mathematical model

A series of mathematical models based on the free volume theory were formulated. These models allow the prediction of the effect of blending polymers with each other, or of adding a plasticiser to a polymer (Wood, 1958):

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

(1)

Where T_g, T_{g1} and T_{g2} are the glass transition temperatures in Kelvin of the compound, polymer and plasticizer respectively, and w_1 and w_2 are the mass fractions of the polymer and plasticiser respectively. Plasticiser efficiency can be quantified by the extent to which a plasticiser reduces the T_g of the polymer (Gordon & Taylor, 1952).

Kelly & Bueche (1961) and Couchman (1963) revised the Gordon and Taylor model by considering the effect of thermal expansion on T_g. The latter authors derived the following equation:

$$\ell n\, T_g = \frac{w_1 \Delta C_{p1} T_{g1} + w_2 \Delta C_{p2} T_{g2}}{\Delta C_{p1} T_{g1} + \Delta C_{p2} T_{g2}}$$

(2)

where the symbols have the same meaning as for equation (1) and ΔC_p is the increment of heat capacity of the pure components at their respective T_g's in °C.

Gibbs-DiMarzio theory

The Gibbs-DiMarzio theory assumes that the experimental glass transition is a kinetic manifestation of an underlying, thermodynamic, second-order phase transition. This theory provides a framework for predicting the effect of variables such as molar mass, plasticiser content, cross-link density and mechanical deformation on T_g (Mark *et al*, 2004).

3.6.3 Factors influencing plasticisation

Plasticisation occurs only as a result of an increase in free volume which permits an increase in the motion of a polymer's molecules. Free volume can be increased from three sources, namely:

- The motion of the chain ends
- The presence of a side chain
- The motion of the main chain.

Increasing the above-mentioned motions can increase free volume by:

- Increasing the number of end-groups by lowering the molecular mass
- Increasing the number or length of the side chain
- Increasing the chain movement by including segments of low steric hindrance and low molecular attraction
- Addition of a compatible compound with a lower molecular weight
- Increasing the temperature.

Thermal properties of plasticised polyvinyl alcohol blends

Jang *et al.* (2003) studied the plasticizer effect on the melting and crystallisation behaviour of PVOH. A blend of glycerine and PVOH granules was dried in a vacuum oven at 80 ^{o}C for 1 h. The PVOH-glycerol mixture was then extruded using a Plasticorder single-screw extruder (L/D =25) at 210 ^{o}C. The thermal properties were characterised using a DSC from 30 to 250 ^{o}C at a heating and cooling of 20 ^{o}C per minute. Jang *et al.* (2003) found that the melting temperature decreased with increasing amount of glycerine. This suggests that an increase in the amount of glycerine increases the segmental mobility of PVOH chains and reduces the crystallinity of the polymer. Figure 6 below shows the effect of increasing the glycerine content on the melting point of partially hydrolysed PVOH.
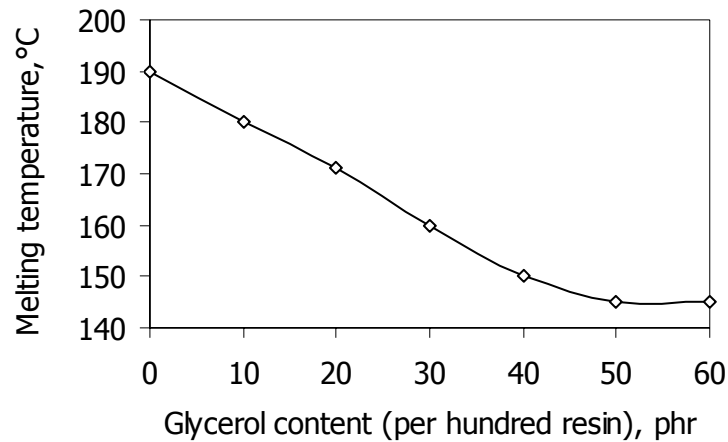
Figure 6: **Effect of glycerol on the DSC melting peak temperature of partially hydrolysed PVOH (Jang *et al.,* 2003)**

Effect of increasing plasticiser mass on the Young's modulus

Young modulus also known as the modulus gives an indication on the stiffness of a material. It is determined from stress-strain curves. Figure 7 shows that as the mass of plasticiser in the PVC is increased, the Young's modulus decreases.
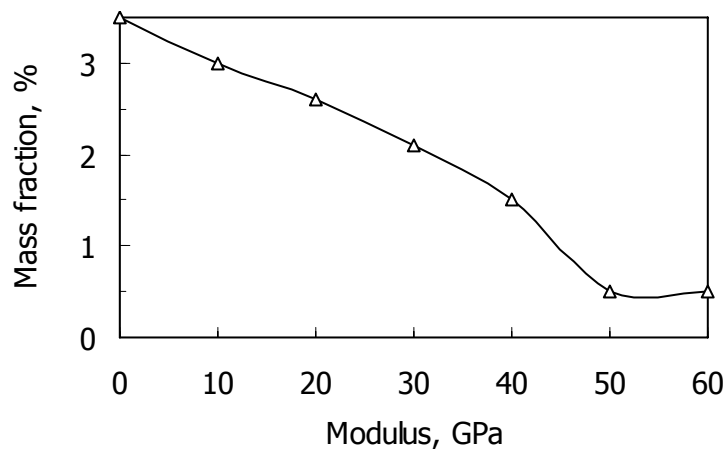

Figure 7: **Schematic illustration of the effect of plasticiser addition on the Young's modulus of a polymer**

3.7 Lubricants

Lubricants are additives used in polymer processing to modify the rheology of polymer melts. They are divided into external and internal lubricants. The most common lubricants are: synthetic and natural waxes, low-molecular-weight polyethylene, and metallic stearates.

External lubricants are used mainly to eliminate external friction between the polymer and the metal surface of the processing equipment. Internal lubricants improve the internal flow characteristics of a polymer, adding to the wetting properties. Many lubricant systems act as both internal and external lubricants (Hay *et al.,* 2000).

Internal lubricants contribute to the polymer matrix's reduced melt viscosity and improved flow, thereby allowing faster production rates. External lubricants allow the molten polymer mix to flow better at the polymer/processing equipment interface, resulting in better surface appearance and gloss. External lubricants can also contribute to the finished product's "antiblock" and "slip" properties.

From a practical viewpoint, internal lubricants have a high degree of compatibility with the polymeric matrix, whereas external lubricants have a limited degree of compatibility, i.e. they tend to migrate to the surface of the polymer, thereby contributing to a degree of slip between the polymer matrix and the processing equipment surface (Hay *et al.,* 2000).

A number of lubricants have been used in the processing of investment moulding compounds: stearic acid, synthetic wax, beeswax and paraffin waxes (Horton, 1988).

Waxes as lubricants

Waxes are short- to long-chain organic compounds, e.g. hydrocarbons, that crystallise easily. Waxes can be either extracted from beeswax and vegetable raw matter, or manufactured from petroleum feedstocks (Hay *et al.,* 2000).

Types of waxes and their properties

Candelilla and carnauba waxes are extracted from vegetable matter. They have a number of different properties that make them useful in industry. Candelilla wax is moderately hard and slightly tacky with relatively low thermal expansion, i.e. less solidification shrinkage than hydrocarbon waxes. Carnauba has a lower thermal expansion than candelilla wax and is very hard, non-tacky and brittle.

Beeswax has properties similar to those of microcrystalline wax. These types of waxes are, however, subject to supply shortages and are very expensive compared with hydrocarbon waxes (Horton, 1988). There are three main types of waxes manufactured from petroleum feedstocks, namely paraffin, microcrystalline and synthetic wax. The three types differ with respect to their molecular weight, the nature of branching and cost. The differences in the chemical, economic and physical properties of these waxes are presented in Table 6.

Table 6: **Chemical, economic and physical properties of hydrocarbon wax (Horton, 1988)**

Wax	Chemical, economic and physical properties
Paraffin	Straight-chain hydrocarbon
	Melting point: 49 -71°C
	Soluble in benzene and warm alcohol
	High molecular weight
	Cost-effective
	Poor heat resistance
Microcrystalline	Branch-chain hydrocarbon
	Melting point: 60-89°C
	Higher molecular weight than paraffin wax
	More costly than paraffin wax
	Fair heat resistance
Synthetic wax	Straight-chain hydrocarbon
	Low molecular weight
	Higher melting point: 100-110°C
	Good heat resistance

Application and function of waxes

Commercially, waxes are available in slab and powder form, depending on the application. Low cost, high lubricity and low melt viscosity are the main properties that make wax a valuable organic material in industrial applications (Horton, 1988). Waxes are applied in a number of industrial fields and offer the functions shown in Table 7.

Table 7:   Applications and functions of waxes (Horton, 1988)

Application	Functions
Adhesives, hot melts	Viscosity adjuster, lubricants, surface hardening
Building	Bitumen modifier and anti-graffiti treatment
Candles	As a fuel, and for light
Cosmetics	Binders and consistency regulators for ointments, creams, pastes lipsticks, etc.
Electrical and electronics industries	Release agents, insulating materials, etching bases
Medicines and pharmaceuticals	Moulding and release agents in dental laboratories and surface hardening of pills
Plastics	Lubricants, release agent, pigment carriers (master batch)
Investment casting industry	Moulding and release agents in investment casting, surface hardening and strengthening

3.8   Filled polymers

3.8.1 Filler-polymer interaction

The type of filler-polymer interaction determines the mechanical properties of a wax pattern. There are basically three different polymer-filler interactions, namely:

- No interaction between the filler and the polymer. This is the typical situation when the polymer is highly non-polar. In this case, the filler acts merely as an extender and its presence weaken the material.

- The polymer wets the filler surface. This will be the case when the polymer has an affinity for the filler surface. A physical bond will exist between the polymer and the surface of the filler (Shenoy, 1999) and good mechanical properties are possible.
- A true chemical bond forms between the filler and the polymer. This increases the strength of the mechanical properties to an even greater extent (Shenoy, 1999).

3.8.2 Factors affecting polymer-filler interaction

Filler content

Owing to the differences in densities, it is more appropriate to express filler content in terms of volume fractions than on a mass basis. The tensile strength decreases rapidly when the filler content exceeds a critical volume concentration. The presence of filler also increases the melt viscosity of moulding compounds. This can cause processing problems during injection moulding (Bierwagen, 1972).

Wettability

For effective bonding to occur between the filler and the polymer, there should be good wetting. The wetting of a solid by a liquid depends upon the interfacial energies between the solid, liquid and vapour phases. Wetting can be determined using the Young's equation (Zisman, 1963). This relates contact angle measurements. This is shown in Figure 8.
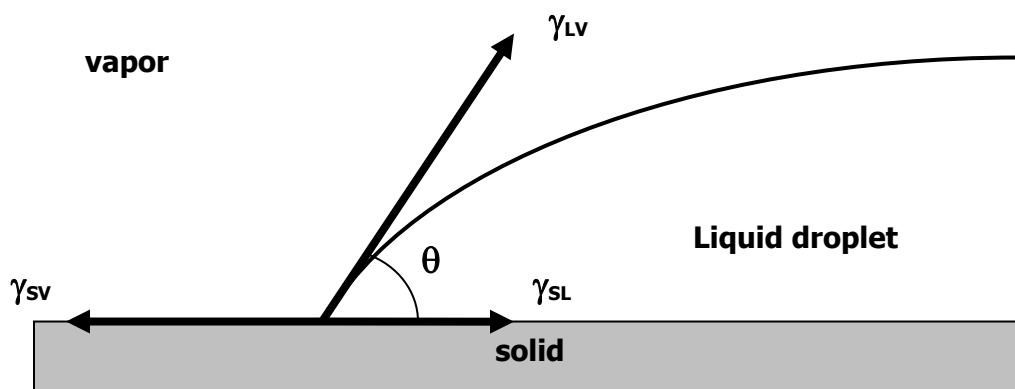

Figure 8: **Contact angle when a liquid drops onto a solid surface (Zisman, 1963)**

Where γ_{LV} is the liquid-vapour interfacial tension, is θ the contact angle, γ_{SV} is the solid-vapour interfacial tension, and γ_{SL} is the solid-liquid interfacial tension.

The contact angle of a liquid drop onto a flat solid is given by the equation below:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}$$

(3)

The wettability theory states that for good wetting to occur, the filler (substrate) surface tension γ_{SV}, or its critical surface energy, should be greater than the surface tension of the wetting agent (polymer) (i.e. $\gamma_{filler} > \gamma_{polymer}$). In other words, $\cos \theta = 1$ or θ is equal to 0°.

Filler surface

The micro-configuration and friction of the filler surface play an important role in filler-polymer interaction. Rough filler surfaces offer more adhesion to polymers than smooth fillers, but smooth fillers are more easily wetted than less regular surfaces. Smooth fillers often have undetected absorbed layers of water and contaminant on their surface which affects the degree of adhesion. For perfect wetting to occur there should be no voids in the filler surface (Davis, 1971).

Filler surface treatment

Filler surface treatment is essential to enhance interfacial bonding and thereby the mechanical performance of filled-polymer systems. The surface treatment process involves surface cleaning and the use of modifiers and coupling agents. A coupling agent is a polymeric compound that forms a bond or attaches itself between a polymer matrix and the filler. Coupling agents are added because, in most cases, fillers are not compatible with the polymers (Edward, 2002).