

3 EXPERIMENTAL

3.1 Experimental design

The objective of this work was to establish the effect of starch source, plasticiser content and blending on the mechanical properties of thermoplastic maize starch. The experimental design used in this study for binary and ternary mixtures is shown in Figure 9. The corners of the triangle represent the pure components, the sides of the triangle represent binary systems and the inside ternary mixtures. The formulations tested in this study are shown as dots in this diagram. The mechanical properties, structure, water resistance and biodegradability of the chosen blends as a function of time were investigated.

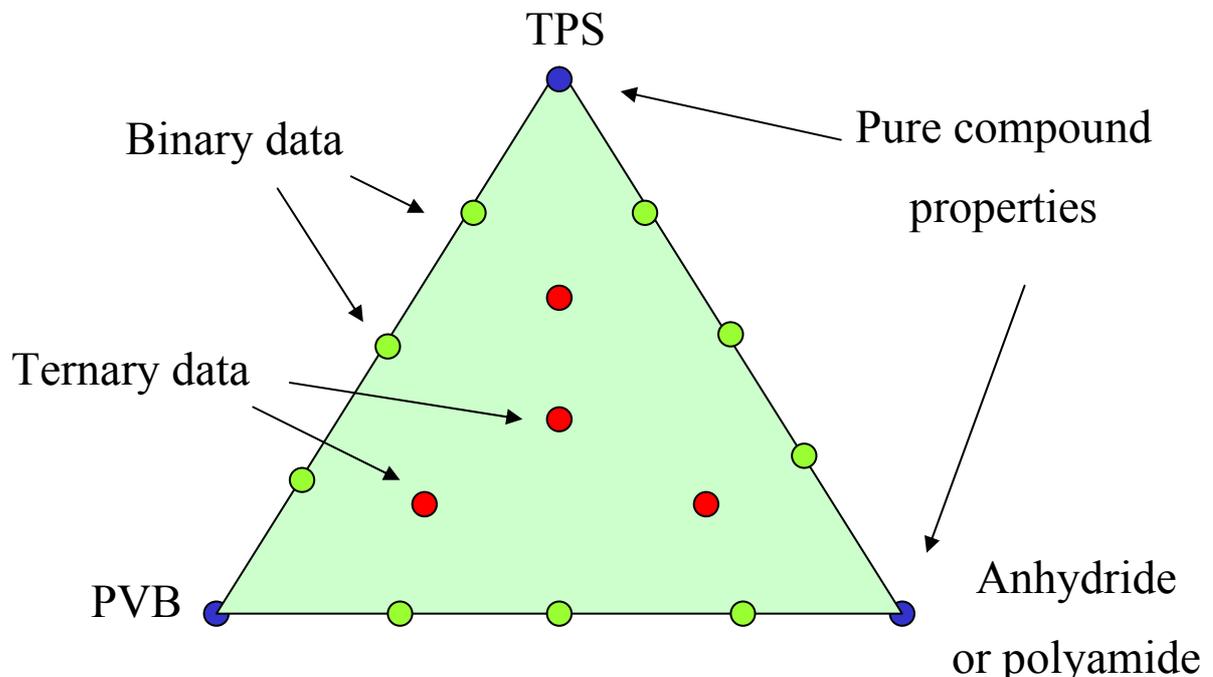


Figure 9: Experimental design

Using the experimental design (Figure 9) as a guide, the following was investigated:

1. Thermoplastic starch: Effect of starch source and type on the mechanical properties
2. TPS-PVB blends
3. PVB-polyamide blends
4. TPS-PVB-anhydride blends

5. TPS-polyamide blends
6. TPS-PVB-polyamide blends

The effect of the starch source on the mechanical properties was investigated. Further, the effects of blending TPS with PVB and polyamides on the processability, mechanical properties with ageing, structure, water resistance and biodegradability were investigated. Each system is discussed separately in the sections that follow. The overall conclusion is given in the last chapter of the thesis.

3.2 Materials

The effect of starch type was evaluated using locally manufactured maize starches supplied by African Products. The different types of starch that were evaluated in this work are given in Table 2.

Table 2: Amylose:amylopectin ratios of native maize and tapioca starch

Type of starch	Trade name	% Amylose	% Amylopectin	Form
Normal	Amyral cornstarch	26	74	Crystalline
Waxy	Amyral waxy	1	99	Crystalline
High amylase	HiMaize™	70	30	Crystalline
Tapioca		21	79	Crystalline

Normal Maize, Waxy and HiMaize™ are granular maize starches that are extracted from three different maize hybrids. The addition of urea and glycerol at varying concentrations was evaluated in order to establish the processing window and the effect on the mechanical properties of thermoplastic starch. The processing aids that were evaluated in this work are given in Table 3.



Table 3: Additives and processing aids

Additive	Supplier	Function
Stearic acid	Protea Industrial Chemicals	External lubricant
Glycerol monostearate (GMS)	Protea Industrial Chemicals	External lubricant
Epoxidised soya bean oil	Protea Industrial Chemicals	External lubricant
Precipitated silica (Vulkasil S)	Bayer	Flowing agent
Urea	Lion Bridge	Plasticiser
Glycerol	Protea	Plasticiser

The standard thermoplastic starch formulation was blended with other synthetic polymers in order to improve mechanical properties, water resistance and processability. The polymers used for blending with thermoplastic starch are given in Table 4.

Table 4: Polymers used for blending with TPS

Material	Trade name	Supplier
Euremelt hot adhesive polyamide	Eurelon 2140 (E2140)	Vantico
Euremelt hot adhesive polyamide	Eurelon 2138 (E2138)	Vantico
Engineering polyamide	Grilon CF 62 BSE	EMS-Chemie
Polyvinyl butyral	Recycled PVB	Vest Designs

Vest Designs supplied the recycled PVB that was used in this work. It consisted of shredded off-cuts from the manufacture of automotive windscreens. The objective of this work was to investigate the properties of blends of thermoplastic starch with recycled PVB.

Polyvinyl butyral (or PVB) is a resin usually used for applications that require strong binding, optical clarity, adhesion to many surfaces, toughness and flexibility. It is prepared from polyvinyl alcohol by reaction with butyraldehyde. PVB is used primarily in the manufacture of laminated safety glass for use in, e.g., vehicle windscreens and buildings. In the event of the glass shattering, the PVB interlayer acts as an energy absorber, holds broken glass

fragments together and prevents shard formation. The PVB used in safety glass comprises typically 55–70% PVB, with 30–45% plasticiser. The standard plasticiser for windscreen laminates is tri-ethylene glycol di-2-ethyl hexanoate, but others, e.g. dibutyl sebacate, may also be used.

Euremelts

Euremelt is the Vantico trade name for a group of thermoplastic copolyamides for use as hot-melt adhesives in many different applications and industries. Euremelt polyamides are based mainly on dimer fatty acids, which are made by a dimerisation process of unsaturated vegetable fatty acids. Such dimer acids, together with other diacids and certain aliphatic diamines, result in the desired polyamides by a polycondensation process. The properties of the polyamides can be modified separately according to special requirements through the choice of suitable raw materials. All polyamide types are more or less compatible, so that finished products can be adapted to suit the intended application.

Euremelt 930 and the “1000-series” are tough-hard, and the other products have high flexibility, some even at very low temperatures down to -30 °C. Euremelt polyamides are solvent-free and show good adhesion to a variety of dissimilar substrates, including steel, aluminium, wood, PVC and other plastics. They differ in softening point, viscosity, hardness, open time and specific adhesion properties. Euremelt polyamides are used in the wood, furniture, shoe, electrical, automotive, textile, packaging and other industries as adhesives or sealants for joining, sealing or fixing. In many cases they are used without further modification, but they can be formulated with fillers or other resins to meet special requirements.

3.3 Sample Preparation

Sample preparation includes all the processing steps necessary to convert granular starch into thermoplastic pellets, such as mixing, extrusion, injection moulding and cutting.



Figure 10: Papenmeier high-speed mixer

The first step in preparing thermoplastic starch is to prepare a free-flowing mixture that can be fed into the extruder. This is done with a high-speed mixer. In this study batches were prepared using a 50 ℓ Papenmeier mixer, shown in Figure 10.

The moisture content of the native starch powder was determined using a Mettler moisture analyser at 120 °C for 30 minutes. This information was used to adjust the amount of water that was to be added in the formulation. The starch with all the other powdered additives was placed in the mixer; mixing was initially done at 1 000 r/min. The plasticisers (glycerol and water) were slowly added to the starch blend through a funnel placed at the top of the mixer. The mixer was run at a speed of 3 000 r/min for 30 minutes. The temperature in the mixer was maintained at 55 to 65 °C by adjusting the speed and the flow rate of the cooling water through the jacket. At these temperatures, minimal plasticiser losses are anticipated. To avoid caking and plasticiser loss, the temperature was kept below 65 °C. The mixer was stopped after 30 minutes to allow the mixture to cool to a temperature below 40 °C. Precipitated silica was added and mixing was performed for one minute.

Extrusion of starch is used in the manufacture of many food products. It is also used to make industrial products, such as pre-gelatinised starch and modified starches. As such, extrusion is nothing new. For the conversion of granular starch into thermoplastic starch, starch gelatinisation must be achieved with the minimum deterioration in the molar mass. For this

reason shear should be applied gradually in the presence of water and plasticisers to protect the starch from degradation. At high water contents, the extrudate tends to foam and the die temperatures must be kept below 100 °C. The aim is to obtain thermoplastic starch pellets that are uniform in shape, size and mass. These pellets flow well in the hoppers of secondary processing equipment, such as injection moulders. Even if foamed pellets could be made in a uniform size and shape, they would be too light to flow well.

The thermoplastic starch was prepared by extrusion. The use of an extruder ensures mechanical breakdown of the starch granules into thermoplastic starch by shear stress and heat. A Berstorff twin-screw extruder, 45 mm co-rotating, L: D=30, and a Rapra single-screw extruder, 25 mm, L: D=24, were used for preparing thermoplastic starch and its blends.

The Berstorff twin-screw extruder has two vents which divide the barrel into three equal sections. It was fitted with a three-hole spaghetti die and was run between 100 and 200 r/min.



Figure 11: Rapra single-screw extruder

The Rapra single-screw extruder (Figure 11) was fitted with a single-hole die. The maximum allowable electrical current is 10 A. The screw speeds were set to obtain a current of 7,5 A. The barrel has three temperature-controlled zones. The die is also temperature controlled. The bulk of the experiments done in this study were compounded on this extruder. The Rapra single-screw extruder was operated at 30 r/min.

After extrusion, the resulting strands were granulated using a pelletiser, while the lumpy extrudates were ground into smaller particles using a grinder. The pellets were conditioned at 30 °C at a relative humidity of 60% before blending.

The resulting thermoplastic starch was made up of: 67,5% HiMaize, 15% glycerol, 15% water, 1,5% stearyl alcohol and 2,5–3% precipitated silica.

Blends containing TPS, polyamide and/or PVB were prepared by extrusion using a 25 mm single-screw laboratory extruder with an L/D ratio of 25. An extruder was employed in order to use high shear and temperature to gelatinise the starch and to melt-mix the two polymers into a blend. The resulting extrudate was air-cooled, cut into pellets and conditioned at a temperature of 30 °C at a relative humidity of 60%. The compositions of the binary and ternary blends used in this work are given in Tables 5, 6 and 7.

Table 5: Composition of the binary blends investigated

TPS, mass %	PVB/Polyamide, mass %
100	0
92	8
78	22
50	50
22	78
8	92
0	100

Table 6: Composition of the TPS-PVB-E2140 ternary systems

Description	TPS, mass %	PVB, mass %	Anhydride, mass %
TPS 6	100	0	0
Eu 10	66.8	16.6	16.6
Eu 12	33.3	33.3	33.3
Eu 11	16.6	16.6	66.8
Eu 9	16.5	66.8	16.6

Table 7: Composition of the TPS-PVB-anhydride ternary systems

TPS, mass %	PVB, mass %	Anhydride, mass %
78	11	11
50	25	25
39	38	25
25	50	25
11	64	25

Tensile specimens, conforming to ASTM D638m, were injection moulded using an Engel 3040 screw-type injection moulder (Figure 12). Injection moulding involves the rapid filling of a fluid polymer into a specific mould. The injection-moulded tensile specimens were conditioned at 30 °C at a relative humidity of 60%.



Figure 12: Engel 3040 screw-type injection moulder

3.4 Characterisation

3.4.1 Tensile tests

The tensile properties of a material provide a measure of the resistance to elongation or breaking when subjected to stretching forces. The stress-strain rate of most materials is time dependent, therefore the speed at which the stress is applied must be taken into consideration. The same force applied slowly may result in the sample yielding, leading to higher resistance to breakage. With an increase in temperature, thermoplastic material becomes less rigid. The change in rigidity is, however, not continuous when T_g and T_m transitions are encountered.

In this work, standard specimens were of Type V conforming to ASTM D638m. As stated above, tensile specimens were injection moulded using an Engel 3040 screw-type injection moulder. The tests were performed at specified time interval using a Lloyds Instrument, operated at a velocity of 50 mm/min. The tensile tests were conducted at room temperature on the same day to avoid a variation in results due to changes in temperature and humidity. Five replicates were performed for each formulation.

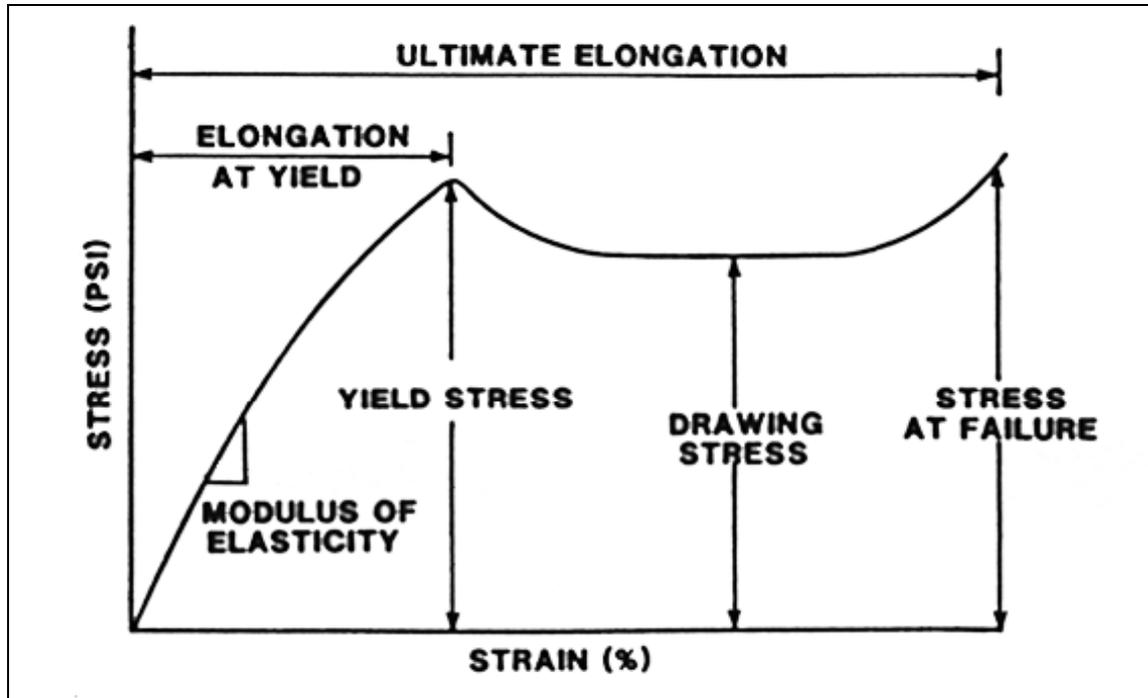


Figure 13: Typical tensile stress-strain curves for plastics

These tensile properties provide an indication of the mechanical performance of the materials. A typical stress-strain curve for a thermoplastic is shown in Figure 13. Points of interest from this graph are:

1. Young's modulus – This is the initial slope of the stress versus strain curve.
2. Stress at break – This corresponds to the loading or stretching force applied to a sample when it breaks.
3. Strain at break – This is the ultimate elongation of a sample at a breaking point.

3.4.2 Dynamic mechanical analysis (DMA)

The dynamic mechanical analysis (DMA) was done on a TA Instruments DMA 2980 machine. Cut-offs from the tensile specimens were conditioned for at least 30 days at 30 °C and 60% RH. The DMA data were determined in bending mode (single cantilever clamp) at a frequency of 10 Hz and a heating rate of 1 K/min in a temperature range from –20 to 100 °C.

The DMA measures the viscoelastic response of the material as a function of temperature and frequency. In particular, the glass transition temperatures of the blend can be determined from the position of the maximum in the $\tan \delta$ versus temperature curve. The modulus of a polymer can be monitored against the frequency of the oscillating deformation of a sample bar at different temperatures. The response of a viscoelastic material will be out of phase with the imposed deformation by an angle, δ . Two different moduli are detected for such a viscoelastic material: firstly, the storage modulus, E' , is related to the in-phase response and represents the recoverable elastic energy. Secondly, the loss modulus, E'' , corresponds to the out-of-phase component of the response. It characterises the fluid-like aspect of the material and thus indicates the portion of the deformation energy that is dissipated by viscous flow. The ratio of the two moduli equals the *dissipation factor* (damping), $\tan \delta = E''/E'$. Both E' and E'' show rapid changes near the glass transition temperature, giving rise to a characteristic peak in $\tan \delta$. The location of this peak in the temperature is usually taken to be the glass transition temperature.

The microscale morphology of the polymer system profoundly affects the glass transition temperatures (T_g). Miscibility can be ascertained by considering the effect of blend composition on the T_g values. Miscible blends show a single T_g intermediate between those

of the parent polymers, whereas two separate T_g's indicate immiscibility. Shifting or broadening of the transition peak occurs in the case of partially miscible systems [Thermo Corsaro & Sperling, 1990].

3.4.3 X-ray diffraction (XRD)

The diffraction of X-rays by matter is a tool that is applied to crystalline materials. X-rays can be described as electromagnetic radiation of short wavelengths and high energy. The range is from 10⁻⁴ nm to 10 nm. The X-rays used in diffraction studies are in the region of 0,05 to 0,25 nm [Skoog & Leary, 1992].

When X-rays interact with the matter, they may be scattered. In a crystal the scattering centres or atoms are located at fixed positions and distributed in a regular way. The diffraction angles (θ) are related to the interplanar distance of the crystal sheets. Bragg's equation relates the spacing between the successive planes and the angle of the incident X-ray beam where constructive interference occurs:

$$2d = n\lambda/\sin\theta$$

where θ is the angle of the incident beam, n is an integer, λ is the wavelength of the incoming X-ray and d is the interplanar distance in the crystal that is characteristic for a given crystal matter (Skoog & Leary, 1992; Jenkins, 1981; Williams, 1987).

XRD analysis was performed on a Siemens D-501 automated diffractometer.

3.4.4 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is commonly used for the investigation of polymer fracture surfaces and blend morphology. The advantages of this technique are its rapid range of accessible magnifications and its depth of field. The current specimens were investigated as follows: the dumbbell test specimens were cryogenically freeze-fractured using liquid nitrogen. This involves freezing the sample in liquid nitrogen, followed by manual breakage to obtain a clean fractured surface, which was then coated with gold. SEM was performed on specimens that had been conditioned for at least 30 days at 30 °C and 60% RH. Low-magnification SEM images of gold-coated samples of fracture surfaces were obtained on a JEOL 840 SEM.

Enzyme erosion tests were performed by immersing thermoplastic starch blends in a solution of alpha amylose. Alpha amylose is an enzyme that digests carbohydrates. After 30 days in this enzyme solution, structural changes that might have occurred were investigated using SEM.

3.4.5 Water resistance

Tensile specimens that had been aged for 30 days were immersed in water at ambient temperature. Tensile tests were performed at seven-day intervals.

3.4.6 Melt flow index

The melt flow index is determined by extruding a material from the barrel of a plastometer under preset conditions of temperature and load. Timed segments of the extrudate are weighed and the extrudate is calculated in g/10 min and recorded. In this study the melt flow index was measured at a load of 2,16 kg at temperatures varying from 120 °C to 160 °C. The plastometer consists of an extrusion plastometer operating at a fixed temperature. The thermoplastic material, which is contained in a vertical cylinder, is extruded through a die by a piston with a known weight.