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TENSILE PROPERTIES OF THERMOPLASTIC STARCH AND ITS BLENDS WITH POLYVINYL BUTYRAL AND POLYAMIDES

By

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ABSTRACT

TENSILE PROPERTIES OF THERMOPLASTIC STARCH AND ITS BLENDS WITH POLYVINYL BUTYRAL AND POLYAMIDES

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Starch is a natural polymer occurring in the seeds, tubers and stems of many plants, including maize. It is a mixture of two polymers: linear amylose and highly branched amylopectin. The ratio and the molar masses of the two polymers depend on the starch source, giving rise to different starch properties. Thermoplastic starch (TPS) was obtained by gelatinising a dry-blend mixture of maize starch, water, plasticisers and additives in a single-screw laboratory extruder. The TPS formed is a translucent amorphous material that could be shaped into pellets and injection-moulded into a variety of articles, just like conventional plastics [Shogren *et al.*, 1994].

The advantages of TPS are that it is cheap and fully biodegradable. However, because of its hydrophilic nature, its properties and dimensional stability are influenced by moisture (humidity). It is also not easily processed like conventional plastics and the freshly moulded material ages, i.e. its properties change over time. The latter is caused by retrogradational structural changes which include helix formation and the crystallisation that occurs above the glass transition temperature [Myllärinen *et al.*, 2002]. The unacceptable physical and processing properties of TPS were improved by blending with other polymers.

The objective of this work was to determine the effects of water and glycerol content and the starch source or type on the mechanical properties of maize-based TPS. In addition, the effect of gypsum filler and polyamides or polyvinyl butyral (PVB) as modifying agent was also investigated. The PVB was based on material recycled from automotive windscreens.



As with the thermoplastic starch, the thermoplastic/polymer blends, e.g. polyvinyl butyral, were also prepared using a single-screw extruder. After pelletisation, the materials were conditioned at 30 °C and a relative humidity of 60%. Tensile test specimens were prepared by injection moulding. Samples were characterised using X-ray diffraction (XRD), scanning electron microscopy (SEM), dynamic mechanical analysis (DMA) and tensile testing. The effect of environmental conditions (temperature and humidity or water submersion) on the ageing of the samples was investigated using tensile properties as a measure.

Initial extrusion and moulding trials revealed that the TPS compounds were very difficult to process. Difficulties were encountered with feeding the dry blends into the compounding extruder. The moulded samples adhered strongly to the mould walls, especially the sprue part. These problems were overcome by adding 2,5% precipitated silica to improve the flowability of the dry blends and stearyl alcohol at ca. 1,5% as a processing aid. The latter performed as an external lubricant and mould-release agent. Nevertheless, for some compositions it was also necessary to use ‘Spray-and-Cook’ as mould-release agent during injection moulding.

The results show that HiMaizeTM, a high-amylose maize starch, provided the best properties in TPS and its blends. Further improvements in properties were obtained by blending with low-molecular-weight hot-melt adhesive-grade polyamides (Euremelt 2138 and 2140), engineering polyamide (EMS Grilon CF 62 BSE) or low amounts of PVB. The properties of all the compounds investigated were affected by moisture content and also by ageing.

The TPS-PVB blends showed highly non-linear composition-dependence. SEM and DMA revealed a phase separation for all the TPS-PVB blend compositions investigated. The tensile properties were negatively affected by ageing in a high-humidity environment and they deteriorated rapidly when the samples were soaked in water. Synergistic property enhancement was observed for a compound containing 22% thermoplastic starch. It featured a higher tensile strength, showed better water resistance and was significantly less affected by ageing. At higher PVB levels, the property dropped to values that were lower than expected from the linear blending rule.

Keywords: Thermoplastic starch; polyvinyl butyral; polyamide, blends; plasticiser; glycerol



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DEFINITIONS

| | |
|------------------------------|--|
| Ageing | Changes over time of the structure and material properties of plastic materials |
| Amylomaize starch | Starch extracted from the maize mutants particularly rich in amylase |
| Biodegradable | Capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds or biomass in which the predominant mechanism is the enzymatic action of micro-organisms, that can be measured by standardised tests, in a specified period of time, reflecting available disposal conditions |
| Compostable | Capable of undergoing biological decomposition in a compost site as part of an available programme, such that the plastic is not visually distinguishable and breaks down to carbon dioxide, water, inorganic compounds and biomass at a rate consistent with that of known compostable materials (e.g. cellulose) |
| Glass transition | Change in the polymeric material from a brittle, glassy state to a more flexible and rubber-like material |
| Glass transition temperature | Characteristic temperature at which the glass-to-rubber transition of a polymeric state occurs |
| Plastic | An organic substance, which may be synthetic, semi-synthetic or natural, formed by a polymerisation reaction. Such a material is capable of being moulded by the application of heat and pressure |
| Plasticiser | A substance or material incorporated into a polymer to increase its flexibility, workability or distensibility. A plasticiser may reduce the melt viscosity, lower the temperature of second-order transition or lower the elastic modulus of the product |
| Semi-crystalline polymers | Polymers with a partially crystalline ordered structure |



| | |
|------------------------|--|
| Thermoplastic material | A material that becomes soft and is easily shaped when heated, and in which the process can be repeated without any appreciable change in material properties taking place |
| Thermosetting material | A material that becomes hard when heated and cannot be softened afterwards by further heating |
| Viscoelastic polymers | Polymers having properties of both liquids and solids |
| Waxy starch | Starch partially rich in amylopectin, extracted from cereal mutants |



LIST OF ABBREVIATIONS

| | | |
|---------------|---|--|
| DMA | = | dynamic mechanical analysis |
| DSC | = | differential scanning calorimeter/calorimetry |
| GMS | = | glycerol monostearate |
| MFI | = | melt flow index |
| PBS | = | polybutylene succinate |
| PBSA | = | polybutylene succinate adipate |
| PCL | = | polycaprolactone |
| PHB | = | polyhydroxy butyrate |
| PVB | = | polyvinyl butyral |
| RH | = | relative humidity |
| SEM | = | scanning electron microscope/microscopy |
| $\tan \delta$ | = | loss factor (loss tangent) |
| TGA | = | thermogravimetric analysis |
| TMA | = | thermomechanical analysis |
| TNO | = | Netherlands Organisation for Applied Scientific Research |
| TPS | = | thermoplastic starch |
| XRD | = | X-ray diffraction |
| EMS | = | Grilon CF 62 BSE |



1 INTRODUCTION

Since their inception, plastics have undergone numerous modifications and improvements to the extent that they can now compare favourably with other applied engineering materials. Plastic materials can be modified with ease by the addition of a variety of additives and fillers to give desired end-use properties. However, their use has been limited by their non-biodegradable nature. In this context they have been considered environmentally unfriendly. Most countries are working on reducing the amount of plastic waste by means of recycling, but this has proved to be unsuitable and uneconomical for certain end-use applications. This global environmental awareness has caused an interest in the development of polymers that will fragment or degrade into benign by-products under composting environments. The use of renewable resources such as starch is considered a cheap way of developing biodegradable materials [Averous *et al.*, 2000]. The main challenge is to make the properties of such a material comparable to those of conventional polymers.

Synthetic biodegradable polymers have already been developed. They are mainly synthetic aliphatic polyesters, such as polycaprolactone, polyhydroxyvalerate, polyhydroxybutyrate and polylactic acid. These polymers degrade due to enzymatic hydrolysis of the ester linkage caused by microbial attack. There are various production methods. Polycaprolactone is polymerised from monomers derived from fossil fuels. Polylactic acid is polymerised from monomers produced from renewable resources via fermentation. Polyhydroxyvalerate and polyhydroxybutyrate are synthesised in bioreactors; microbes feed on the carbohydrates and form polymers inside their cells which are used as an energy-storage medium.

The main disadvantage with synthetic biodegradable polymers is their high cost [Averous *et al.*, 2000]. These polymers are sold at prices that are four to ten times the price of polyethylene. This is due to the complexity of the technology involved in the production of these materials. Cargill-Dow has emerged as one of the front-runners with their NatureWorks polylactic acid. Polylactic acid has the advantage that it is based on natural resources and, because the polymer is made under controlled conditions, it has good properties. However, although the polymer is made from renewable resources, the energy required for manufacturing means that only 20–50% less fossil fuel is required to produce the polymer [Bastioli *et al.*, 1994].

Control over the composition and structure of polymers from renewables is not possible. The main disadvantages with these polymers are their dominant hydrophilic character, critical ageing and their poor mechanical properties.

Thermoplastic starch (TPS) is a translucent amorphous material that looks and feels much like conventional plastics. It is obtained by ‘gelatinising’ native starch in the presence of suitable plasticisers, such as water or glycerol [Shogren *et al.*, 1992]. A controlled extrusion-compounding process can achieve this: applying gentle heating and high shear causes the starch granules to absorb the plasticisers, allowing them to melt at a reduced temperature without decomposing [Van Soest & Vliegenthart, 1997]. The TPS exiting the extruder is a viscous melt; it can be shaped into pellets that can be injection moulded into a variety of articles, just like conventional plastics.

Plain thermoplastic starch is inexpensive and biodegrades quickly. However, there are some drawbacks: it has limited water resistance; its properties and dimensional stability are influenced by moisture (humidity); it does not process as easily as conventional plastics; and the freshly moulded material ages, i.e. its properties change over time [Shogren & Jusberg, 1992]. The latter changes are caused by retrogradation. [Kim *et al.*, 1997], (Retrogradation is the change in properties of thermoplastic starch-based materials with time, caused by recrystallisation during ageing.) The structural changes include helix formation and crystallisation, which occur above the glass transition temperature.

The unacceptable physical and processing properties of thermoplastic starch can be improved by blending with other polymers. To retain biodegradability, it is conventional to use other biodegradable polyesters, such as poly- ϵ -caprolactone, polyhydroxy butyrate and polylactic acid [Bastioli., 1998]. In this study we considered the use of polyamides and recycled polyvinyl butyral as TPS modifying agents.

In South Africa large quantities of polyvinyl butyral (PVB) are recovered from scrap windscreens through a mechanical delamination process. There is, however, very little interest in recycling this post-consumer waste stream owing to a lack of suitable markets for it and the contamination with residual glass fragments. Consequently, it is disposed of in landfill or incinerated. Nevertheless, some PVB is recycled but this is, in the main, limited to recovered factory off-cuts.

The compatibility of PVB with other polymers is important as it is likely that the end-use for the recovered PVB will be in a PVB-polymer mixture, especially where the PVB has a useful effect on the blend properties.

The objective of this work was to determine the effects of water and glycerol content and of the starch source or type on the mechanical properties of maize-based thermoplastic starch (TPS). In addition, the effects of gypsum filler and polyamides or polyvinyl butyral as modifying agent were investigated. The polyvinyl butyral was based on material recycled from automotive windscreens.

1.1 Scope of the work

The aim of this project was to develop a low-cost, locally sourced and biodegradable starch-polymer blend for injection-moulding applications. To this end, the properties and processing of blends of thermoplastic starch (TPS), obtained from locally produced maize starches, with polyvinyl butyral (PVB) and/or polyamide were investigated. Varying the composition of the formulation should make it possible improve the processing behaviour and to modulate the properties of TPS from a very flexible material to a brittle one. The effects of the amylose:amylopectin ratio and of the plasticiser content on the mechanical properties and processability were analysed. In addition, the effect of blending on the mechanical properties, processability and rheology of the resulting blends was investigated. Finally, the effect of processing, by both single- and twin-screw extruders, on the final blend and blend properties was investigated.



2 LITERATURE REVIEW

2.1 Biopolymers

Biodegradability is dependent on the chemical nature of the material and the constitution of the final product. Biodegradable plastics can be synthetic or natural polymers. Natural biodegradable polymers are based on renewable resources, whereas synthetic biodegradable polymers are petroleum-based. Biodegradation is degradation caused by biological activity, such as enzyme action, which leads to major changes in the chemical structure in a given time period into simple molecules, such as carbon dioxide and water [Billmeyer, 1966].

2.2 Starch structure and properties

Native starch is the term used to describe starch in the form in which it occurs in plants, such as potatoes, wheat, cassava, rice and maize. In plants, starch occurs in the form of granules. The granules vary in shape, size and relative proportions of amylose and amylopectin, depending on the source of the starch. Starch is therefore described by its plant source as cornstarch, potato starch, tapioca starch, etc. [Souza & Andrade, 2001].

Starch is composed of carbon, hydrogen and oxygen in the ratio of 6:10:5 [$C_6H_{10}O_5$], placing it in the class of carbohydrate organic compounds. Starch is considered to be a polymer of glucose, with the linkages between the glucose units being formed as if condensation has taken place. The glucose units are connected through an oxygen atom, connecting through carbon atom 1 of one glucose unit to carbon atom 4 of the next glucose unit, forming a long chain of interconnected glucose units. This linkage of one glucose unit to another one through the C-1 oxygen atom is called the *glycoside bond* [Souza & Andrade, 2001].

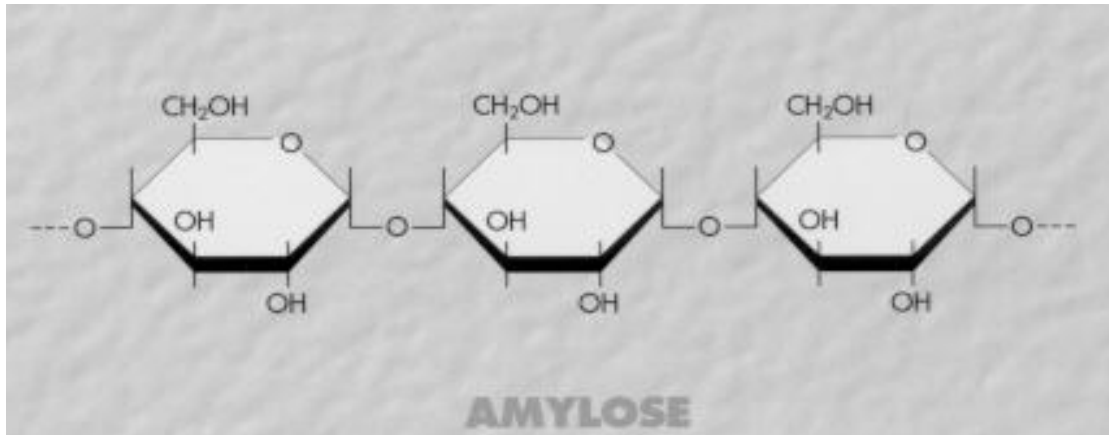


Figure 1: Structure of amylose [African Products, s.a.]

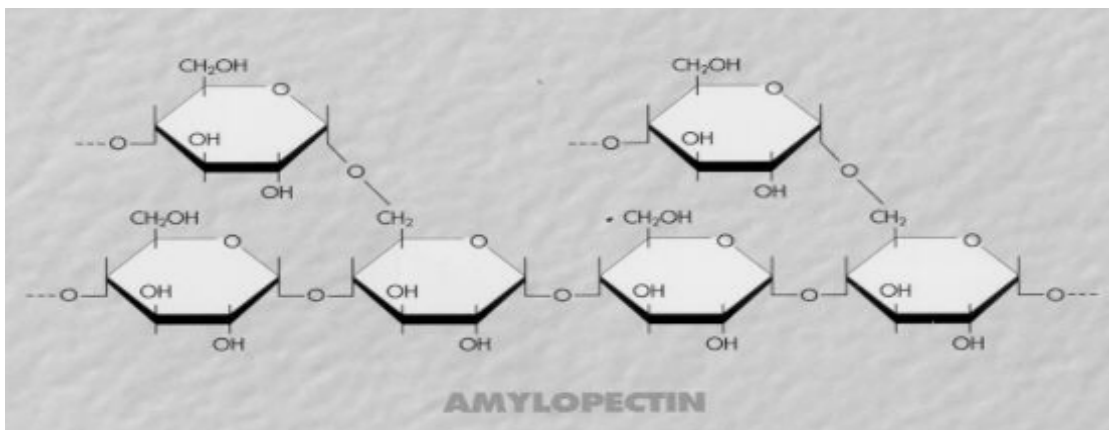


Figure 2: Structure of amylopectin [African Products, s.a.]

Starch in its native state consists of a mixture of two polysaccharides: amylose and amylopectin. Amylose is a linear polymer, while amylopectin is highly branched. The glucose units in amylose are connected to each other through 1-4 linkages [Hulleman *et al.*, 1998]. The relative amounts of these two polymers in a particular type of starch determine the properties of the starch. The molecular structures of amylose and amylopectin are given in Figures 1 and 2 respectively [Bello-Perez & Paredes-Lopez, 1995]. Typical starch compositions are given in Table 1.



Table 1: Composition of potato and maize starches

| Type of starch | Potato | Maize | Waxy maize | High-amylose maize |
|-------------------|--------|--------|------------|--------------------|
| % Amylopectin | 79 | 74 | 100 | 30 |
| DP of amylopectin | 60 000 | 60 000 | 60 000 | 60 000 |
| % Amylose | 21 | 26 | 0 | 70 |
| DP of amylose | 6 000 | 1 300 | - | 1 300 |

DP = Degree of polymerisation, i.e. the number of glucose atoms in the molecule

2.3 Starch gelatinisation

In its native form, granular starch is partially crystalline. When dry starch granules are heated, thermal degradation occurs before the granular crystalline melting point is reached. As a result, starch cannot be melt-processed in its native form. In order to melt-process native starch, the hydrogen bonds holding the starch molecules together have to be reduced. The reduction of starch hydrogen bonding can be achieved in the presence of a solvent, such as water. When starch is heated in an aqueous medium, the phase transition forms an ordered to disordered state called *gelatinisation* [Kim *et al.*, 1997].

The properties of starch in water are the bases on which starch can be melt-processed. When starch is heated with the solvent at a critical temperature, the solvent interacts with the starch hydroxyl groups, thus reducing the hydrogen bonding among the starch molecules. This allows individual chains to move freely relative to each other, thus allowing starch to be melt-processed. The critical temperature at which this phenomenon occurs is called the *gelatinisation temperature* [Willett & Doane, 2002].

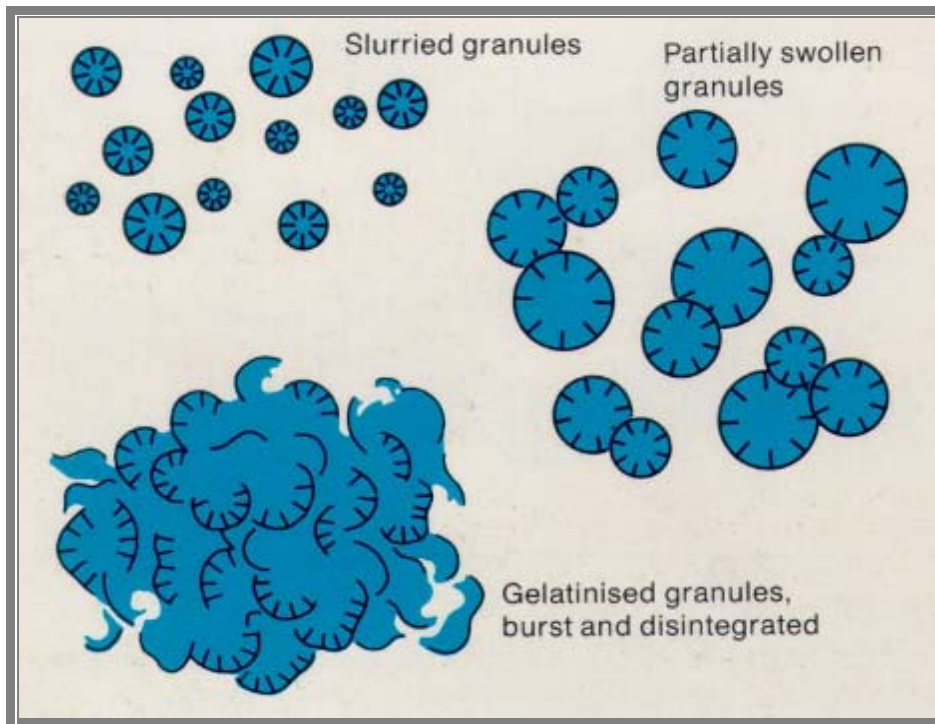


Figure 3: Illustration of the gelatinisation process [African Products, s.a.]

2.4 Starch modification

Starch modifications are carried out in order to provide products with the required end-use properties. These modifications are aimed at changing the gelatinisation characteristics, solids–viscosity relationship, gelling tendency of starch dispersions and hydrophilic character, and at introducing ionic character [Souza & Andrade, 2001].

2.4.1 Modifications aimed at changing the amylose/amylopectin content

Hybrid breeding has been the most successful way of developing starches containing mainly amylopectin. These waxy starches have been available since 1942.

2.4.2 Modification by controlled degradation

This process involves the scission of the starch molecules to fragments of lower molecular weight. Commercially, the conversion is carried out by the action of oxidising agents, acids and/or heat.



2.4.2.1 *Oxidation*

Native starch can be treated with a variety of oxidising agents. The agent most commonly used is sodium hypochlorate. In the first stage of oxidation, the starch chain is hydrolysed into shorter fragments, thus reducing the molecular mass. This results in a reduction in the viscosity of the system. The starch hydroxyl groups are oxidised to aldehyde and ketones. The introduction of the carbonyl group into the amylose molecules reduces retrogradation [African Products, s.a.].

2.4.2.2 *Acid-converted starches*

In this process starch is treated with a mineral acid at low temperature, below the starch gelatinisation temperature, to keep the granules intact. Under these conditions, the acid hydrolyses the starch, breaking the linkages between glucose monomers to yield shorter chains. Hydrolysis initially takes place at the branching points of amylopectin, producing a starch that has a higher proportion of linear molecules. Since the polymer chains have been shortened, the starches have a lower molecular mass than unmodified starches, as well as low viscosities [African Products, s.a.].

2.4.3 Pregellatinisation

Pregellatinised starches are prepared by cooking and drying starch slurries in heated drums or by means of extrusion. Since the granular structure has been disrupted, this process produces starches that swell in cold water [Souza & Andrade, 2001].

2.4.4 Cross-linking

The gellatinisation and swelling properties of the starch granule can be modified by the addition of a cross-linking agent. This is done by reacting a starch with chemicals containing more than one functional group, which are able to react with at least two hydroxyl groups. The most common cross-linking agents used in starch are linear dicarboxylic acid anhydrides (e.g. adipic acid) or phosphates (e.g. phosphorous oxychloride trimetaphosphates) [Souza & Andrade, 2001].

2.4.5 Cationisation

Starch cationisation is performed by chemical means in changing the electrical charge from slightly negative to positive. The cationisation process is done by substituting the hydrogen atoms on the starch molecules with quaternary ammonium chemical groups. The cationic



activity in the starch derivative results from the positive charge on the ammonium ion. The number of cationic groups per glucose molecule determines the degree of substitution. The degree of substitution varies from 0.01 to 0.10 [Valle *et al.*, 1991]. Cationic starches are of large-scale importance in industry due to their affinity for negatively charged substrates (cellulose and other fibres) [Souza & Andrade, 2001].

2.4.6 Acetylating

Starch esterification proceeds either by direct reaction with carboxylic acids or by indirect reaction with carboxylic acid derivatives. Common reagents used in the esterification of starch are acetic anhydride, acetic anhydride-pyridine, ketene, vinyl acetate, acetic acid and acetic anhydride–acid. Direct acid esterification is proton-catalysed, with the formation of a starch ester and water. Indirect esterification uses nucleophilic substitution at the unsaturated carbon atom. Acetylated starches of commercial importance are the derivatives of low substitution, since the process preserves the granular structure of starch molecules [Souza & Andrade, 2001].

2.4.7 Dextrinisation

The action of heat on dry native starch in the presence or absence of a catalyst causes *dextrinisation*. The starch is initially dried to obtain a low moisture content; this is followed by acidification using gaseous hydrochloric acid. The mixture is then heated in an agitated vessel under vacuum. The chemical reaction that takes place during dextrinisation is not clear: it seems that hydrolysis takes place mostly on the 1,4 sites, together with a certain amount of rearrangement to the 1,6 sites [Souza & Andrade, 2001].

2.4.8 Grafting

Starch graft polymers are prepared by initially generating free radicals on the starch which will later serve as micro-initiators for the synthetic monomer. Several free-radical-initiating systems, such as chemical initiation, irradiation initiation and mastication, have been suggested for the preparation of starch grafts. The method chosen is governed by the type of polymer used for grafting and the required end-use properties of the grafted polymer [Chinnaswamy & Hanna, 1990].

2.5 Starch as a thermoplastic material

The use of starch as a plastic material has been recorded in literature since the 1950s. Since then a lot of research has been done on starch, but starch has gained limited applications as a packaging material. The main advantages of starch as a material are its low cost, abundance and availability from agricultural crops. When compared with synthetic polymeric material, starch has two main disadvantages:

1. Starch contains hydroxyl groups, which impart hydrophilic properties to starch. Amylose dissolves in water and amylopectin swells in the presence of water. This means that starch disintegrates in water and loses its properties when exposed to moisture [De Carvalho *et al.*, 2001].
2. Starch in its native form it is not thermoplastic. When it is heated, pyrolysis occurs before the crystalline melting point of starch is reached. Therefore it cannot be melt-processed using conventional plastics equipment [Andersen & Hodson, 2001].

In the literature, various techniques are given for rendering starch suitable for use as a material, such as deconstructing starch (thermoplastic), filling synthetic polymers with starch, blending starch with other thermoplastic polymers and making starch-based nano-composites. [Bastioli *et al.*, 1995].

Thermoplastic starch is formed through the destructuring of the native starch granules by heating at relatively high temperatures, under high shear conditions and with limited amounts of water [Hulleman *et al.*, 1998]. The liquid swells the starch granule and reduces hydrogen bonding and crystallinity in the granule. This results in an increase in molecular mobility and makes it possible to melt-process native starch below its degradation temperature [Van Soest *et al.*, 1996a]. By altering the moisture content and extrusion parameters, thermoplastic products with different properties can be made [Bikiaris *et al.*, 1998].

The amount of water used, in combination with the temperature chosen, has a significant effect on the conversion of starch. Starch conversion can be achieved in two ways. Under excess water, all the crystallites in the starch could be pulled apart by swelling, leaving none to be melted at higher temperatures. Conversion can also be achieved in a limited-water environment, which is the usual condition during extrusion. In the latter process, the swelling

forces are less significant and the crystallites melt at temperatures much higher than the gelatinisation temperature in excess water [Yu and Christie, 2001].

During extrusion, starch is subjected to relatively high pressure (up to 10^3 psi), heat and mechanical shear forces, resulting in gelatinisation, melting and fragmentation. Starch extrusion is carried out at lower moisture contents, from 12% to 16%, which is below the amount of water necessary for gelatinisation. The starch granules are physically torn apart by mechanical shear forces, thus allowing faster transfer of water into the starch molecules. This results in the disruption of molecular bonds and loss of crystallinity, which in turn leads to high molecular mobility, thereby enabling the starch to be processed below its degradation temperature [Avérous *et al.*, 2001]. This means that a mixture of small amounts of gelatinised and melted states of starch, as well as fragments, exists simultaneously during extrusion. Gelatinisation is influenced by variables such as moisture content, screw speed, temperature, feed composition (amylose:amylopectin ratio) and residence time [Yu and Christie, 2001].

2.5.1 Effect of relative humidity

When thermoplastic starch is wetted or exposed to high humidities, absorption of water occurs. Thermoplastic starch is not water resistant and is therefore susceptible to starch ageing, leading to poor mechanical properties. In potato starch, water uptake decreases with an increase in plasticiser content at lower relative humidities, while the opposite has been observed at higher humidities. The effect of plasticiser content on the water uptake of potato starch at varying relative humidities is illustrated in Figure 4 [Van Soest & Vliegenhart, 1997].

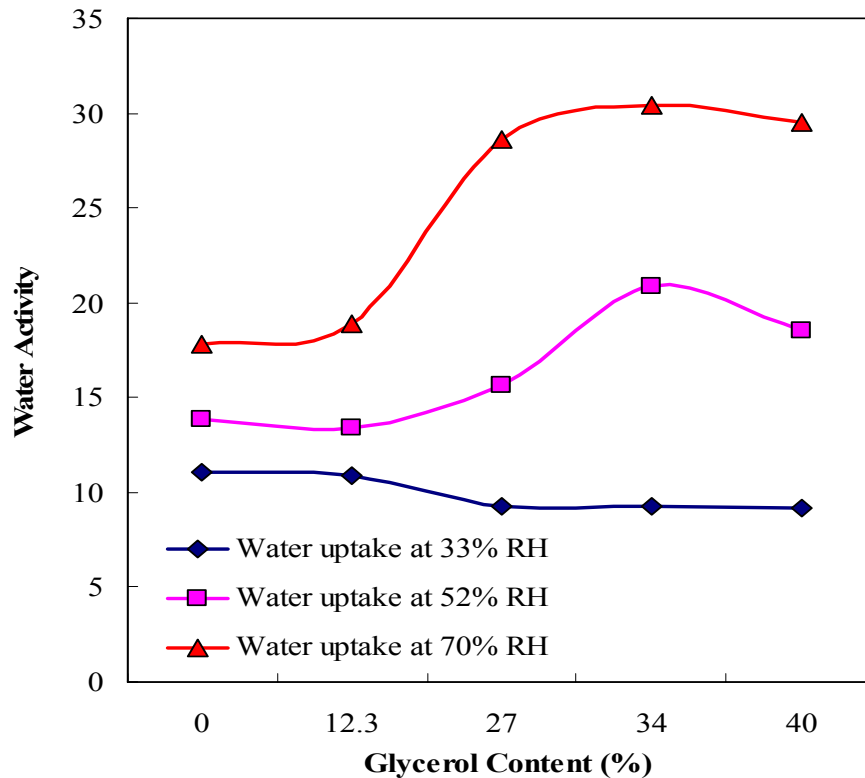


Figure 4: Water uptake as a function of glycerol content and equilibrium relative humidity [Van Soest & Knooren, 1997]

2.5.2 Effect of plasticisers

A plasticiser is a material that is incorporated into a plastic material to increase flexibility, workability or distensibility. Plasticiser molecules penetrate the starch granules, destroying the inner hydrogen bonds of the starch under high temperature, high pressure and shearing. This eliminates starch-starch interactions owing to their replacement by starch-plasticiser interactions. In the literature, other hydrophilic liquids that are used as plasticisers for thermoplastic starch are given; these include glycerol, sorbitol, glycols, maltodextrin and urea. Water is the most common solvent or plasticiser used with starch. Because the plasticiser molecules are smaller and more mobile than the starch molecules, the starch network can be easily deformed without rupture [Yu *et al.*, 1998].

The melting and decomposition temperatures of starch decrease with an increase in plasticiser content. The presence of 2% glycerol monostearate (GMS) in glycerol-plasticised wheat starch reduces the melt viscosity and improves the water sensitivity. The decrease in melting and decomposition temperatures for cornstarch plasticised by glycerol is illustrated in Figure 5 [Liu *et al.*, 2001].

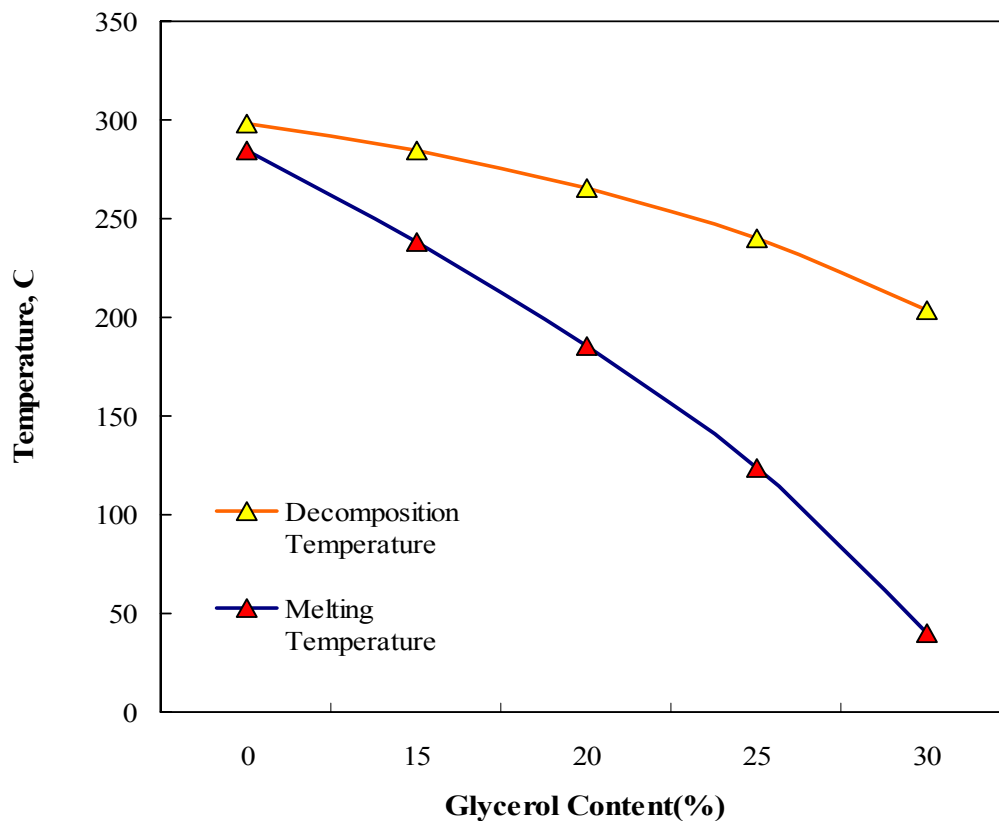


Figure 5: Effect of glycerol on the processing window of cornstarch [Liu *et al.*, 2001]

The span between melting temperature (T_m) and decomposition temperature (T_d) represents the processing window. The processing window extends with an increase in the amount of glycerol [Liu *et al.*, 2001]. Figures 6 and 7 illustrate the effect of glycerol on the tensile strength and elongation-to-break of thermoplastic starch. Tensile strength decreases with an increase in the amount of glycerol, while elongation-at-break increases with an increase in glycerol content within a certain range. Beyond this range, elongation-at-break decreases with an increase in glycerol content. At high glycerol concentrations, the interactions among molecules are very weak because they have replaced the interactions among starch-starch macromolecules. The addition of a small amount of boric acid leads to an increase in mechanical properties, especially elongation-at-break. Boric acid reacts with both glycerol and starch to form an interconnected network [Yu *et al.*, 1998].

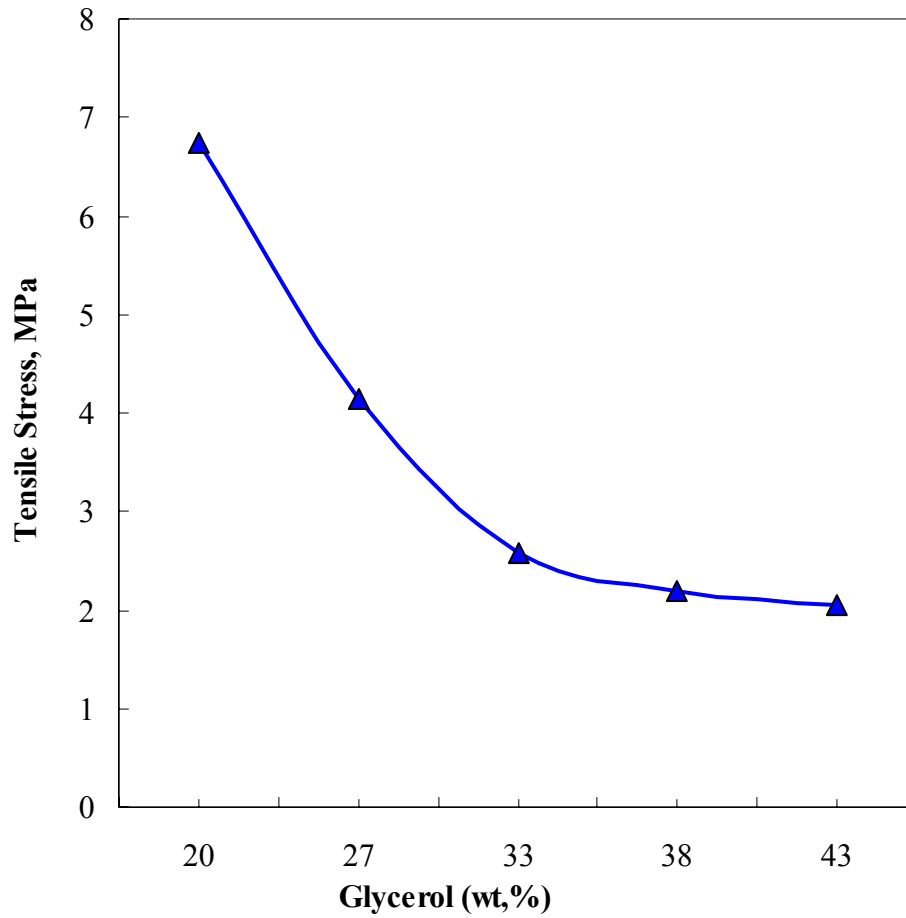


Figure 6: Schematic illustration of the effect of glycerol content on the tensile strength of potato starch [Yu *et al.*, 1998]

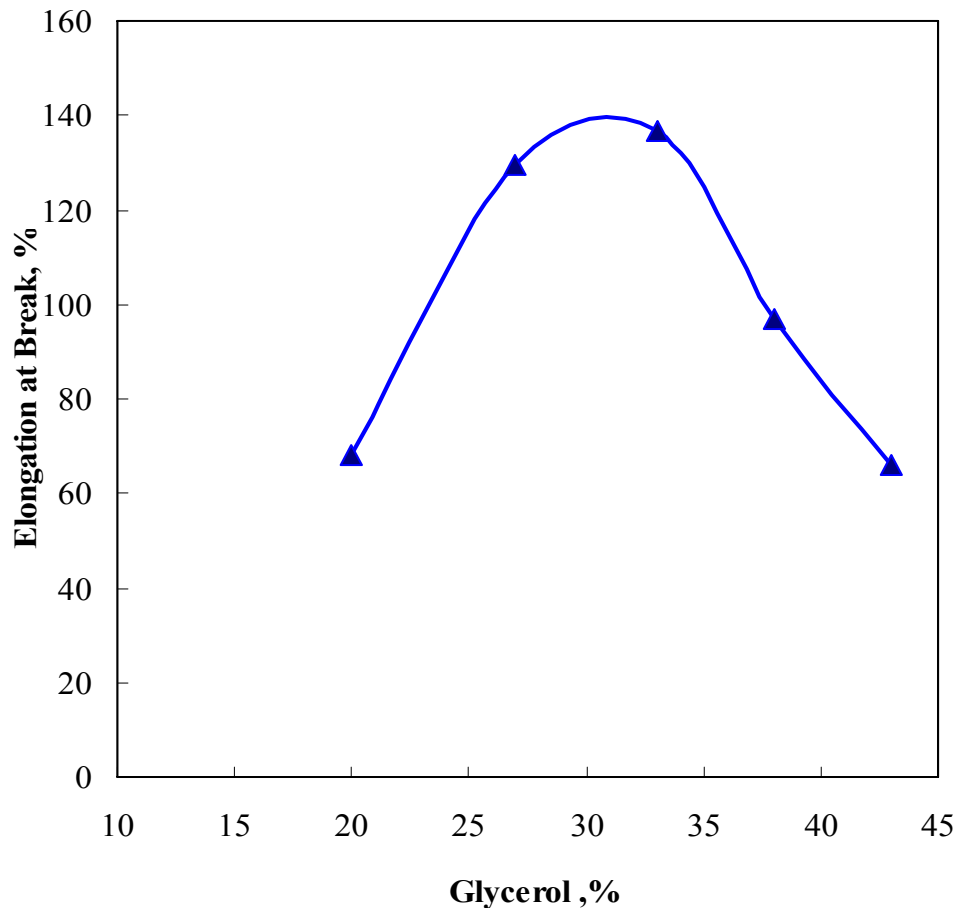


Figure 7: Schematic diagram illustrating the effect of glycerol content on elongation-to-break [Yu *et al.*, 1998]

Water and glycerol are the most common plasticisers used in the processing of thermoplastic starch. The type of plasticiser used influences the glass transition temperature (T_g) of TPS [Van Soest *et al.*, 1996b]. However, urea and various glycols (triethylene glycol, polyethylene glycol and glycerol), and mixtures of these, have also been used as plasticisers for the gelatinisation of cornstarch. At lower urea:glycol ratios (0.2:1), the starch extrudates are brittle and shatter like glass, despite the fact that the T_g was lowered to 50 °C. An increase in the urea:glycol ratio in the starch ribbon from 0.2:1 to 0.6:1 decreased the tensile strength from 19 MPa to 7 MPa and caused a slight decrease in elongation. The mechanical properties of the ribbons remained stable with time at 50% relative humidity, showing that the glass transition is below room temperature where the system is in thermodynamic equilibrium. Urea also disrupts starch hydrogen bonding, so no retrogradation occurs. Starch ribbons containing high levels of urea were stiff due to the low mobility of urea as compared with

ribbons containing high levels of glycols. This is due to the higher mobility or fluidity of glycols [Khalil *et al.*, 2002].

2.5.3 Effect of ageing

One of the disadvantages of thermoplastic starch is its brittleness which is caused by its relatively high glass transition temperature (T_g) and the lack of a sub- T_g main chain relaxation area. During storage this brittleness increases due to retrogradation. *Retrogradation* is the change in mechanical properties of thermoplastic starch caused by a recrystallisation process. The recrystallisation process is caused by the tendency of macromolecules to form hydrogen bonds during the expulsion of water and/or other solvents. This process can be divided into the recrystallisation of amylose and the irreversible crystallisation of amylopectin. Since the reversible recrystallisation of amylose is slower, retrogradation is referred to as the long-term recrystallisation of amylopectin [De Graaf *et al.*, 2003].

Glycerol-containing starch plastics have been shown to recrystallise into various crystalline structures during storage, resulting in changes in mechanical properties. The amylose content of TPS forms the E_h -type of crystallites which are not stable and which rearrange after several days into the V_h -type of crystallites. Like amylopectin, amylose also forms the B-type of crystallites during storage [Van Soest *et al.*, 1996c]. The amount of single helical structures (E_h and V_h) is dependent on the amount water used during processing rather than on the amount of total plasticiser (glycerol and water). During ageing the amount of single helical structures does not increase and therefore retrogradation is caused by the recrystallisation into double helical structures (B-type crystallinity). The formation of B-type crystallinity is dependent on the plasticiser content. The higher glycerol-containing extruded material takes up more water during storage and therefore increases the rate of retrogradation [Van Soest & Vliegenhart, 1997].

2.6 Starch-filled plastics

Granular starch can be mixed with molten thermoplastics without gelatinising the starch. In this case the starch acts as filler for the polymer, reducing the total material cost. Because the starch granules are not gelatinised or plasticised, the processing has to be done below the thermal degradation temperature of the starch. Since the starch retains its granular form, it does not contribute to the mechanical properties of the mixture, and these properties decrease

with increasing starch content. Many examples can be found in the literature, for both biodegradable and non-biodegradable synthetic polymers [Shogren *et al.*, 1993]. This technique is only commercially viable if the saving in materials cost is greater than the added processing cost. Unfortunately, there is an inverse relationship between starch content and material properties. Often, material properties reach an unacceptably low level before a significant cost saving can be made.

2.7 Starch blends

In polymer science, blending is done in order to improve unsatisfactory physical properties of the existing polymer. In starch plastics, moisture sensitivity and critical ageing have made it necessary to associate thermoplastic starch with other polymers. In order to preserve the biodegradability of the final blend, only biopolymers are used. When thermoplastic starch is melt-mixed with any other thermoplastic, the mixture can be considered a polymer blend. Because starch is hydrophobic, it forms compatible blends with polar polymers like polyesters. To retain biodegradability, only biodegradable polyesters such as poly- ϵ -caprolactone, polybutylene succinate adipate (PBSA), polyhydroxy butyrate (PHB) and polylactic acid are often used [Ratto *et al.*, 1999].

Blending starch with degradable synthetic aliphatic polyesters has become a major focus in the development of biodegradable polymers. Wheat thermoplastic starch was found to be not fully compatible with poly- ϵ -caprolactone (PCL) at different ratios of TPS:PCL, with TPS as the major phase of the blend (< 50%). The addition of at least 10% of PCL significantly reduced water sensitivity and dimensional stability. The mechanical properties of the blend are dependent on the plasticiser level in the TPS. For low-plasticised TPS, the addition of PCL resulted in a decrease in the material's elastic modulus, while impact strength improved. For rubbery TPS, the addition of PCL increased the modulus, while the impact strength decreased [Averous *et al.*, 2001]. Application of starch-PCL blends is limited because this material has a melting point of 60 °C and therefore softens at temperatures above 40 °C [Lorcks *et al.*, 2001a, 2001b].

Other polyesters, such as polybutylene succinate (PBS) or polybutylene succinate adipate (PBSA), have been blended with starch to improve the mechanical properties. The rheology of PBSA-TPS blends is better than that of starch on its own. The tensile strength of the blends

was lower than that of the polyester on its own, but was independent of the amount of starch added. The addition of 5% starch reduces the half-life significantly as compared with that of the polyester on its own. The half-life declined with an increase in the starch content. A minimum of 20% starch content was recommended for blending with PBSA [Ratto *et al.*, 1999].

Polyhydroxy butyrate (PHB) is fully compatible with potato TPS. Film formation started with a PHB:starch ratio of 0.3:0.7. The physical properties were found to be maximal at a ratio of 0.7:0 [Godbole *et al.*, 2003].

2.8 Starch-based nano-composites

A recent innovation at TNO (Netherlands Organisation for Applied Scientific Research) is the incorporation of nano-particles into thermoplastic potato starch. Naturally occurring clays are milled, treated with organic cations to separate the particles (intercalation) and incorporated into thermoplastic starch. The starch-based nano-composites can be blended with polyesters to improve their properties. The concept is illustrated in Figure 8:

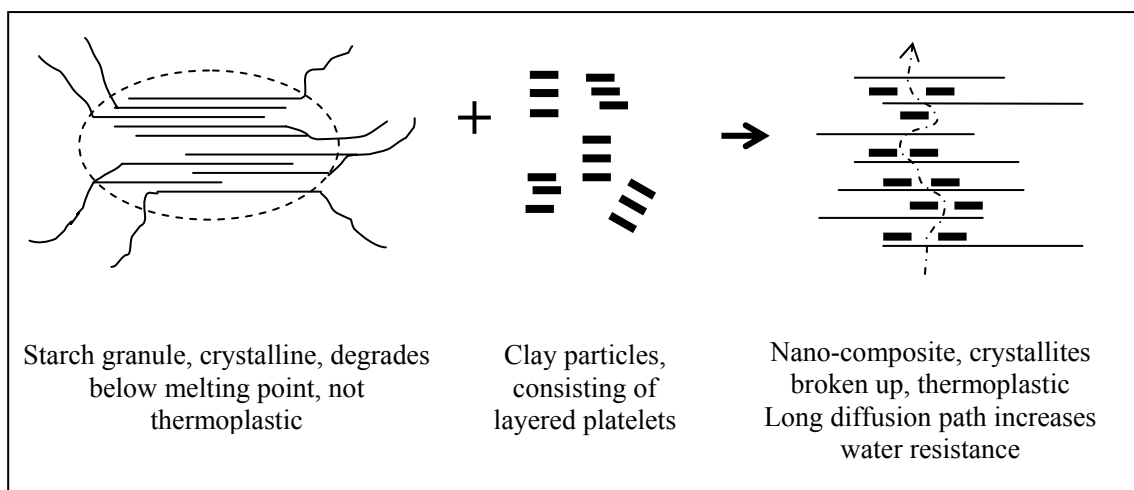


Figure 8: Preparation of a starch-based nano-composite

The presence of the clay improves the starch/plasticiser/polyester blend in the following ways:

- The clay platelets disrupt hydrogen bonding between the starch chains, thereby reducing the crystallinity and making the starch more thermoplastic.

- The platelets increase the length of the diffusion path that the water has to follow to penetrate the material. Therefore the water resistance is improved.
- Some material properties, e.g. stiffness and permeability, are improved by the presence of the clay particles.

This technology has improved one of the main problems associated with starch-based plastics, namely water resistance. It is a major step forward in the development of starch-based plastics. However, all the work has been done on potato starch, and is therefore not relevant to South Africa where only maize starch is produced. Overall, therefore, this project investigated the properties and processing of blends of thermoplastic starch, obtained from locally manufactured maize starches, with polyvinyl butyral (PVB) and/or polyamide for injection-moulded products. The ultimate aim of this work was to develop a cheap, fully biodegradable starch-polymer blend for injection moulding using local resources.

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.

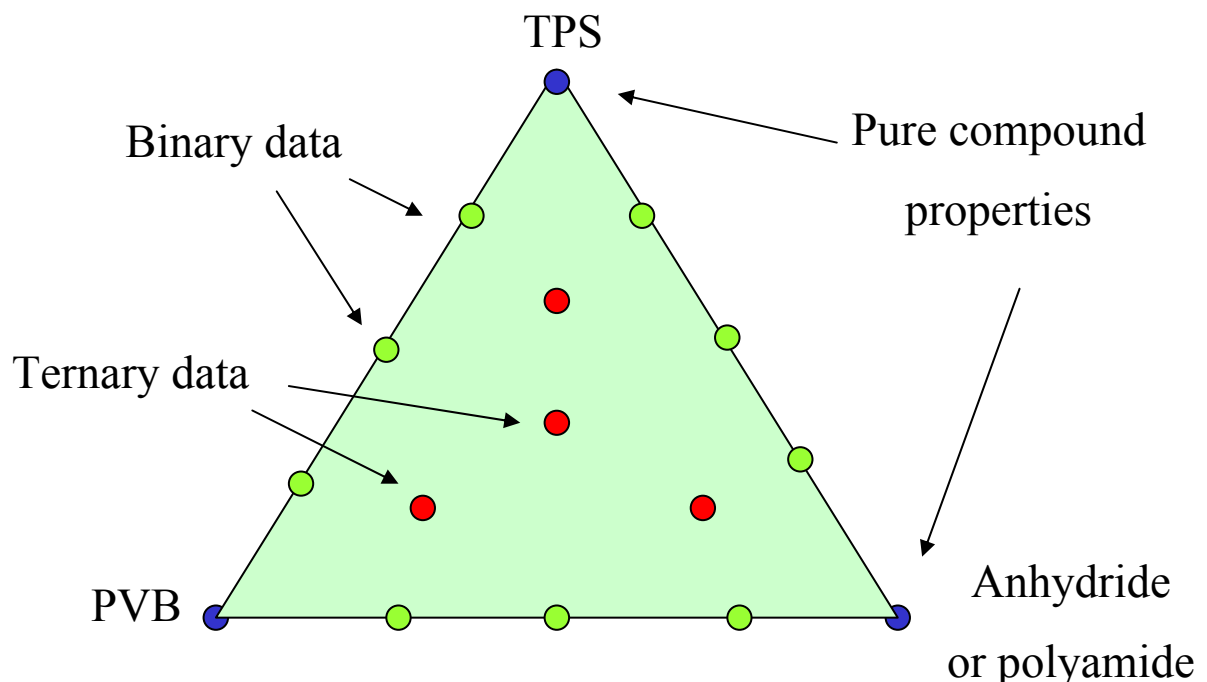


Figure 9: Experimental design

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.

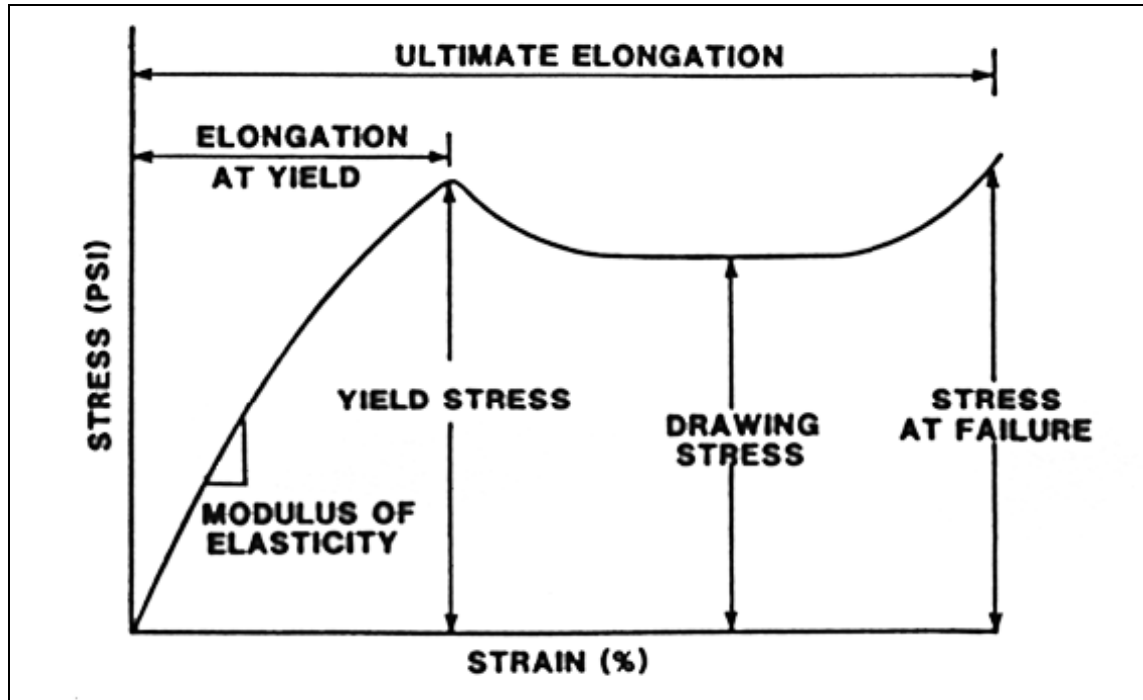


Figure 13: Typical tensile stress-strain curves for plastics

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 Tg'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.

4 RESULTS AND DISCUSSION

The raw data are given in Appendix C as the average values measured together with the standard deviations. Owing to the nature of the materials studied here, the precision of the data is low. For clarity of data trends, the standard deviations are not indicated in the figures presented.

4.1 Thermoplastic Starch

4.1.1 Extrusion

The TPS extrudate obtained using the Berstorff twin-screw extruder was hard, brittle and glassy, even for formulations with a plasticiser content of up to 25%, with barrel temperatures at 100 °C throughout all barrel zones. Different temperature settings were also evaluated along the entire profile. At temperatures higher than 100 °C, the resulting extrudate was light brown in colour and smelled slightly burnt (like caramel). Adding additional water to the mixture yielded a foamed, brittle material. These observations indicate degradation of the starch owing to the high shear generated in the twin-screw machine. Since extrudate with good mechanical properties could not be obtained, the Berstorff twin-screw extruder was not used for the preparation of thermoplastic starch and its blends. Instead, the Rapra single-screw extruder was used throughout this work for the preparation of thermoplastic starch and its blends.

Table 5 provides an overview of the processing window for TPS compounded in the Rapra extruder. Four types of behaviour were observed. At very low water and glycerol contents, the powders were too dry and the material simply degraded in the extruder. At slightly higher water and plasticiser contents, gelation did occur but the resulting melt was too viscous and rapidly caused blocking of the die. At very high levels of water and glycerol, the feed was too wet to be fed into the extruder. It was therefore concluded that suitable, well-gelatinised extrudates were only possible for formulations containing 20 or 25% water, or 15% or less glycerol. However, the mixture containing 15% water and 15% glycerol also performed well.

Note that Figure 8 (Section 2.8) indicates that increasing glycerol content simultaneously decreases the melting point and the degradation temperature of thermoplastic starch. However, the melting point decreases more rapidly with increasing glycerol content and

therefore the net effect is an increase in the processing temperature window [Liu *et al.*, 2001].

Table 8: Processing window of the HiMaize™ TPS formulations using the Rapra single-screw extruder

| | | Water content [% mass] | | | | | | |
|------------------------------|----|------------------------|---------|---------|---------|-----|-----|-----|
| | | 0 | 5 | 10 | 15 | 20 | 25 | 30 |
| Plasticiser content [% mass] | 0 | Burnt | Burnt | Blocked | Blocked | √ | √ | Wet |
| | 5 | Burnt | Burnt | Blocked | Blocked | √ | √ | Wet |
| | 10 | Burnt | Burnt | Blocked | Blocked | √ | √ | Wet |
| | 15 | Burnt | Blocked | Blocked | √ | √ | √ | Wet |
| | 20 | Blocked | Blocked | Blocked | Wet | Wet | Wet | Wet |
| | 25 | Blocked | Blocked | Blocked | Wet | Wet | Wet | Wet |
| | 30 | Blocked | Blocked | Blocked | Wet | Wet | Wet | Wet |

4.1.2 Evaluation of plasticisers

Urea was not found to be a good plasticiser during this study, although it is mentioned as a plasticiser in the literature [Shogren *et al.*, 1992]. Its solubility parameter is not very high and its hydrogen-bonding capability falls well within the range of that of the other plasticisers. The main problem with urea is that its thermal degradation starts just above the melting point (ca. 140 °C). Therefore there is no temperature range in which the urea forms a thermally stable liquid. During extrusion, the extruder blocked at the die zone with the evolution of gas in the extruder, which led to “spluttering” and “shooting” of material from the extruder die. When heated to high temperatures, the urea cross-linked with the starch and this caused the blockage of the extruder. It was not possible to obtain extrusion conditions.

It has been reported that the addition of mineral acids reduces cross-linking [Khalil *et al.*, 2002]. For this reason phosphoric acid was added to some samples during extrusion. Although it did make the extrusion process more stable, the product obtained was brown and had a “burnt” smell. The extrudate was weak and broke easily. The extrusion process was also a health hazard due to the emission of ammonia and carbon dioxide. When the extrusion

temperatures were lowered to below 120 °C, the extrusion process became stable, but the product obtained was not gelatinised sufficiently and was thus quite weak.

Initial extrusion and moulding trials revealed that the TPS compounds were very difficult to process. Difficulties were encountered with feeding the dry blends into the compounding extruder. The addition of precipitated silica produced a free-flowing starch blend which fed without blocking the extruder. It was mixed into the starch/water/plasticiser mixtures just before compounding at levels of 2 to 3%. This yielded a free-flowing mixture for extrusion, preventing lump formation and bridging in the throat of the extruder.

It was found that the TPS produced inside the processing window determined above was almost impossible to mould owing to the very high melt viscosity. Therefore, the addition of lubricants was investigated. The addition of more than ca. 2% epoxidised soya bean oil, stearic acid, magnesium and calcium stearates or glycerol monostearate (GMS) significantly retarded or even prevented gelatinisation of granular starches in the extruder. This was apparent from the poor dispersion of these additives in the final extrudates and this affected the material properties adversely. These additives form thin lubricating layers around the starch granules which may also have retarded the absorption of the water required for gelatinisation. The addition of many of these additives also caused problems with the feeding of material into the single-screw extruder.

Stearyl alcohol added at levels between 1 and 1,5% was found to be the best lubricant, based on visual observations of the flow behaviour during compounding and injection moulding. The addition of 2,5% precipitated silica was necessary to facilitate feeding of the dry blends into the compounding extruder. After considerable trial and effort, the best feeding and processing performance was achieved with the formulation given in Table 9. This was chosen as the base TPS formulation used in this study.

Table 9: Thermoplastic starch base formulation

| Constituent | Mass % |
|---------------------|--------|
| HiMaize™ | 67,5 |
| Glycerol | 15 |
| Water | 15 |
| Stearyl alcohol | 1,5 |
| Precipitated silica | 2,5 |

Extrusion to produce thermoplastic starch aims to gelatinise the starch with the minimum deterioration in the molar mass. For this reason, shear was applied gradually in the presence of water and plasticisers to protect the starch from degradation. The extrusion temperatures at the die zone were kept at a 100 °C to prevent foaming.

4.1.3 Effect of starch source on the mechanical properties

The effect of starch type was evaluated using the TPS base formulation given in Table 6. The effect of ageing on the tensile properties is presented in Figures 14 and 15.

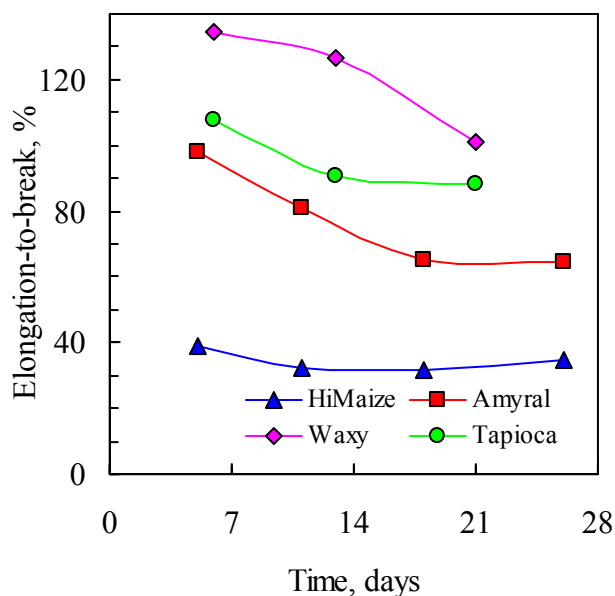


Figure 14: Effect of ageing at 30°C and 60% RH on the elongation-at-break

The TPS compounds based on waxy maize and tapioca starch showed very high shrinkage (> 20%) on ageing. This resulted in gross deformation of the tensile test pieces. The TPS

based on high-amylose maize starch shrank by less than 5%. The linear amylose molecules easily pack closer together, resulting in stronger interactions and hence a higher degree of crystallinity. They also have a lower molar mass and consequently the melt is less viscous. This makes it possible to achieve more complete denaturing of the starch granules. Conversely, these materials, in the liquid state, are also able to crystallise more rapidly to form entangled structures based on crystallites connected by tie molecules. In the high-amylopectin samples, the molar mass is much higher and the molecules are highly branched. The melt viscosity is also much higher, implying that the chain-diffusion coefficients are also much lower. The processing time was apparently too short to allow full chain relaxation and crystallisation during the forming process. Note that the T_g for these samples with a water content of ca. 15% in the moulded state is below 5 °C (Van Soest *et al.*, 1996b). The ageing therefore took place at 30 °C, i.e. above the T_g . This explains the extensive retrogradation and gross deformation (over several days of ageing) of the samples containing high levels of amylopectin.

The mechanical properties of the TPS materials reflect their multi-phase morphology. They form a complex network of completely plasticised starch, recrystallised starch, partially destructured granular starch and intact granular starch (Van Soest *et al.*, 1996b). Obviously, the extent of this morphology development depends on the molecular nature of the starch and the formulation's composition. However, the processing parameters, including the shear rates applied and their duration, have a very significant effect as well. It is clear that the processing freedom available in this project was very limited and it is therefore likely that the properties that were measured are not the ultimate values that could be achieved in the ideal case. In fact, the results may be counter-intuitive as the “best” morphological development was clearly not achievable with the available processing procedures.

The elongation-to-break decreased with a decrease in the amylopectin content. Van Soest *et al.* (1996b) explained that this phenomenon can be attributed to the difference in molecular mass of amylose and amylopectin. The latter has a much higher molar mass and therefore the chains are more entangled in the amorphous network. The samples with a high amylopectin content can be stretched much further before complete chain disentanglement occurs. For TPS from HiMaize, there is a slight decrease in elongation-to-break for the first ten days and thereafter it remains almost constant. A slight decrease in elongation-to-break is also observed

with ageing time for the high-amylopectin starches, which is attributed to retrogradation, i.e. a considerable change in physical properties on ageing.

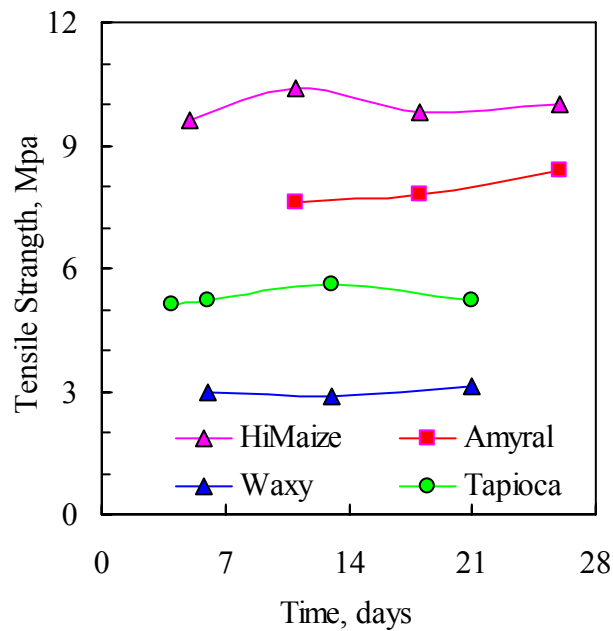


Figure 15: Effect of ageing at 30°C and 60% RH on TPS tensile strength

The tensile strength remained approximately constant for all starch types, but decreased with an increase in amylopectin. Van Soest & Borger [1996] explained this in terms of the differences in structure of amylose and amylopectin, as explained above. The difference in mechanical properties reflects the effects of the differences in starch morphologies resulting from the inherent structure of the starch and the degree of processing applied. Of the starches tested, the high-amylose starch yielded the best tensile properties and was least prone to ageing [Van Soest & Vliegenhart, 1997]. Based on the evaluations performed on the various grades of maize starch with varying amylose:amylopectin ratios, HiMaizeTM showed the best retention of tensile properties with ageing time [Sita *et al.*, 2003]. This is in agreement with the work done by Van Soest & Borger [1996].

The effect of plasticiser content on normal maize starch was determined using the same base formulation. Only the relative proportions of water and glycerol were varied. The results are presented in Figures 16 and 17. Elongation-at-break decreased with ageing time, while tensile strength increased. This is due to the decrease in the number of chains in the amorphous state and the shortening of tie molecules between crystallites over time. The time-dependent behaviour is affected by plasticiser content. The rate of recrystallisation is determined by the

amount of glycerol in the materials. Crystallisation rate increases with an increase in both water and glycerol content [Van Soest & Knooren, 1997].

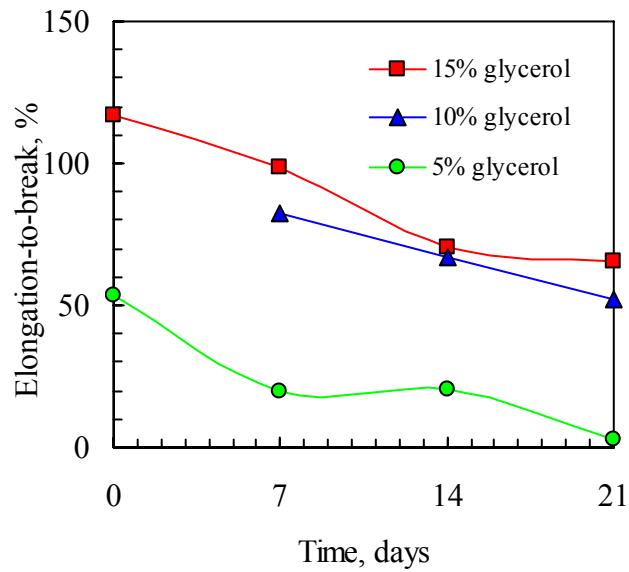


Figure 16: Effect of glycerol content on the breaking strain of normal maize-based TPS aged at 23 °C and 44% RH

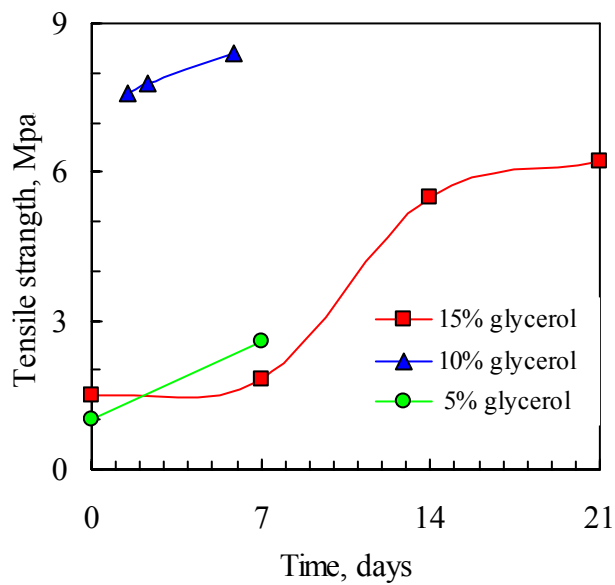


Figure 17: Effect of glycerol content on the tensile strength of normal maize-based TPS aged at 23 °C and 44% RH



4.1.4 Effect of filler

The addition of fillers (anhydride gypsum, mica, vermiculite, silica and talc) to granular starch yielded mixtures that were very viscous, as indicated by the very high torque required for them to be compounded. This is caused in part by (a) the effect that fillers have in increasing the effective viscosity of a suspension, and (b) the reduction in water and in the availability of plasticiser for gelatinisation owing to occlusion inside agglomerates of filler particles. This led to slow gelatinisation, forming a thermoplastic starch that was only slightly plasticised, resulting in high viscosities. For this reason, high torque was required to mix the starch with the filler. Only formulations containing less than 8% filler could be extruded.

In an attempt to overcome this problem, thermoplastic starch was initially prepared and compounded with the filler in a second step. This did not work well with the equipment used in this study. Pre-mixing of thermoplastic starch pellets with powder fillers did not lead to the formation of homogenous mixtures due to the differences in particle size and density of the two components. Secondly, the single-screw extruder used in this work is not really suitable for compounding fillers into polymer melts and therefore samples with poor dispersion of the filler in the polymer were produced.

The results of the extrusion trials done using the Berstorff twin-screw extruder and the Rapra single-screw extruder illustrate that the conversion of granular starch into thermoplastic starch requires the gradual application of shear in the presence of high levels of plasticiser. Excessive shear is harmful to the starch and results in breakage of the polymer chains (reduction in the average molar mass), ultimately leading to brittle materials. Every extruder is unique and therefore the processing parameters, barrel temperatures, screw speeds, etc. should be set up by systematic experimentation.

All TPS compounds showed poor processability during injection moulding, especially the sprue part. This was improved by adding stearyl alcohol at ca. 1,5% as an external lubricant and mould-release agent. Nevertheless, for some compositions it was also necessary to use a mould-release agent during injection moulding. Commercial “Spray-and-Cook” was found to be adequate for this purpose. The processing window for injection moulding was found to be relatively small and had to be determined by trial and error for each composition.

Good mechanical properties were achieved only by using high-amylose starch. Starch high in amylopectin was very difficult to process and showed extensive retrogradation, with samples even cracking spontaneously during ageing. Increasing the glycerol content increased the elongation-to-break but reduced the tensile strength of the TPS compounds.

4.2 TPS-PVB blends

The extrusion temperatures for TPS–PVB blends are presented in Table 10. The extrusion parameters were highly influenced by the composition of the formulation. Higher temperatures were necessary for formulations with high TPS contents.

Table 10: Extrusion parameters TPS-PVB blends

| Polymer Blend | Barrel Temperature, °C | | | |
|---------------|------------------------|------------------|---------------|-----|
| | Feeding zone | Compression zone | Metering zone | Die |
| 100% TPS | 120 | 150 | 150 | 100 |
| 92% TPS | 120 | 155 | 150 | 95 |
| 78%TPS | 120 | 150 | 145 | 94 |
| 50% TPS | 120 | 135 | 130 | 80 |
| 22% TPS | 120 | 140 | 135 | 85 |
| 8% TPS | 120 | 140 | 135 | 85 |
| 0% TPS | 100 | 115 | 115 | 70 |

Injection moulding was again a difficult process: Very high injection pressures were required for blends with high starch contents. As with extrusion, the injection-moulding processing parameters were influenced by the formulation of the blend. For each formulation the optimum settings were those that allowed 100% filling of the mould without warpage and flashing. The injection-moulding parameters are given in Table 11. Sticking in the sprue bush was a problem, despite the inclusion of stearyl alcohol in the formulation. “Spray & Cook” had to be sprayed into the mould after every shot.

Table 11: Injection-moulding parameters for TPS-PVB blends

| Polymer Blend | Barrel Temperature, °C | Injection Pressure, bar |
|---------------|------------------------|-------------------------|
| 100% TPS | 140; 145; 145; 150 | 70 |
| 92% TPS | 125; 130; 130; 140 | 85 |
| 78%TPS | 125; 130; 130; 140 | 105 |
| 50% TPS | 125; 130; 130; 140 | 95 |
| 22% TPS | 125; 130; 130; 140 | 105 |
| 8% TPS | 125; 130; 130; 140 | 110 |
| 0% TPS | 125; 130; 130; 140 | 110 |

The moisture content of the single components and the blends increased during equilibration at 30 °C and 60% RH. For the TPS it was 2,4% and 3,6% after 14 and 30 days respectively. By comparison, the moisture content of the recycled PVB after 30 days was 1,3%, whereas for the blends with 22, 50 and 78% TPS it was ca. 1,8%.

Figure 18 shows the effect of ageing at 30 °C and a humidity of 60% RH on the tensile properties of the TPS-PVB blends. For the neat PVB, the tensile strength and the Young's modulus decrease on ageing owing to the increasing moisture content. Clearly, water also plasticises PVB, lowering its glass transition temperature and its tensile properties. The modulus of the plasticised PVB is rubber-like and decreases from ca. 5 MPa to 1 MPa on ageing (Figure 18).

The tensile strength and modulus of the TPS increased with ageing. However, the neat TPS compound shows a strong decrease in elongation-to-break (ϵ_B) with time. This correlates with an increasing brittleness of these samples and is attributed to the retrogradation of the starch compound [Kim *et al.*, 1997], as also explained above.

With blends, the modulus increases by two orders of magnitude, in a nearly log-linear manner, as the TPS content is increased to 100%. The ϵ_B of PVB and the blends rich in PVB are not much affected by ageing (Figure 18). The blends with 22% or less of PVB have an ϵ_B of less than 40%, i.e. similar to that of the starch-based TPS. The ϵ_B exceeds 200% for blends containing 50% or more of PVB. This suggests that the properties of the continuous phase

approach PVB behaviour down to 50% PVB. In general, the tensile strength of the blends that contain 50% or more TPS is lower than expected from the linear blending rule. However, the 22% TPS compound shows significantly higher values.

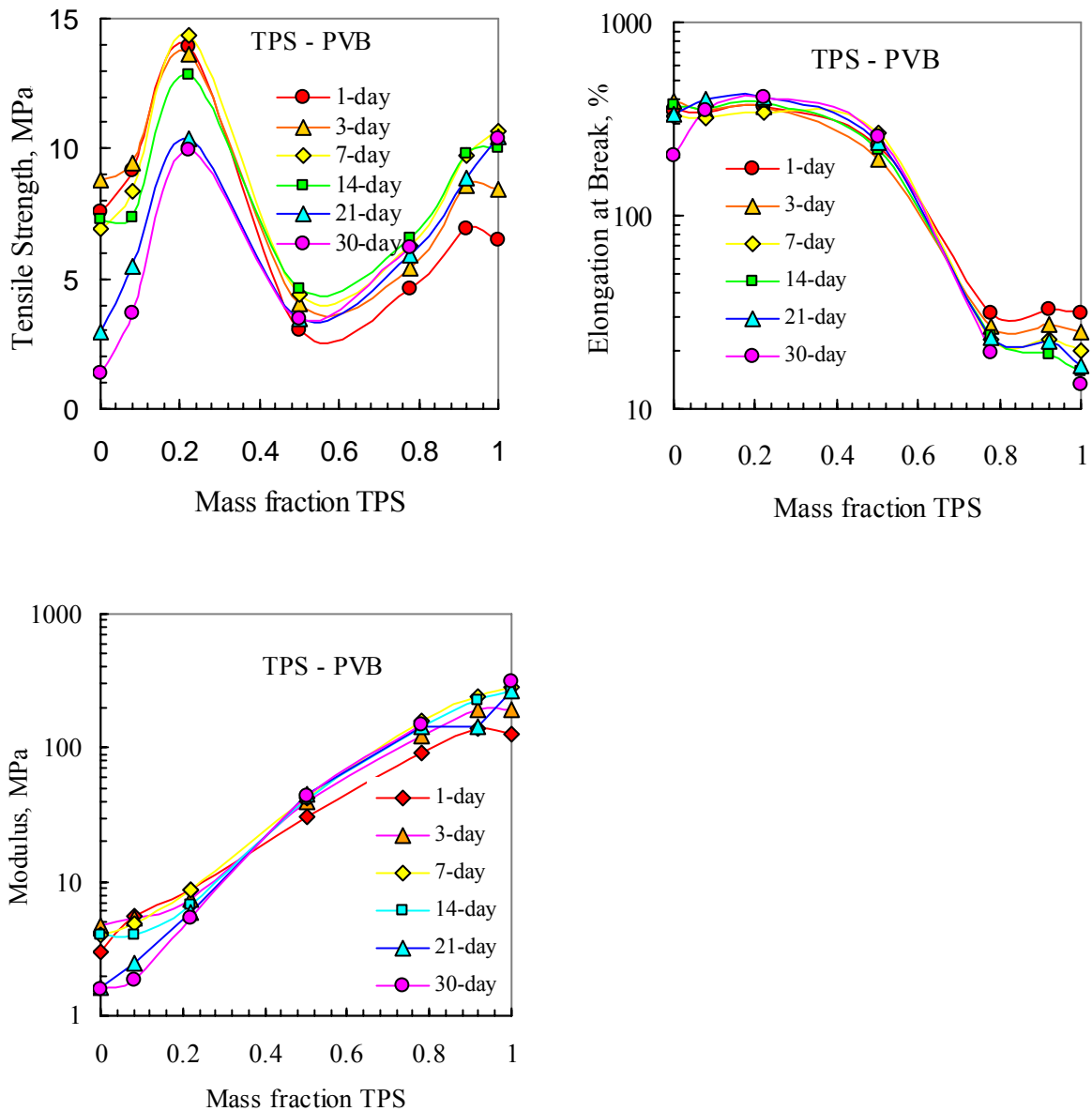


Figure 18: Effect of ageing at 30 °C and 60% RH on the mechanical properties of TPS-PVB blends

Although the compound containing 22% TPS also showed property losses on ageing, it had the best water resistance: Figure 19 shows that it was the only composition tested that retained a significant portion of its tensile strength in the water-soak tests. Noteworthy is the complete

loss of mechanical properties for the blends with high starch contents in which the starch forms the continuous phase.

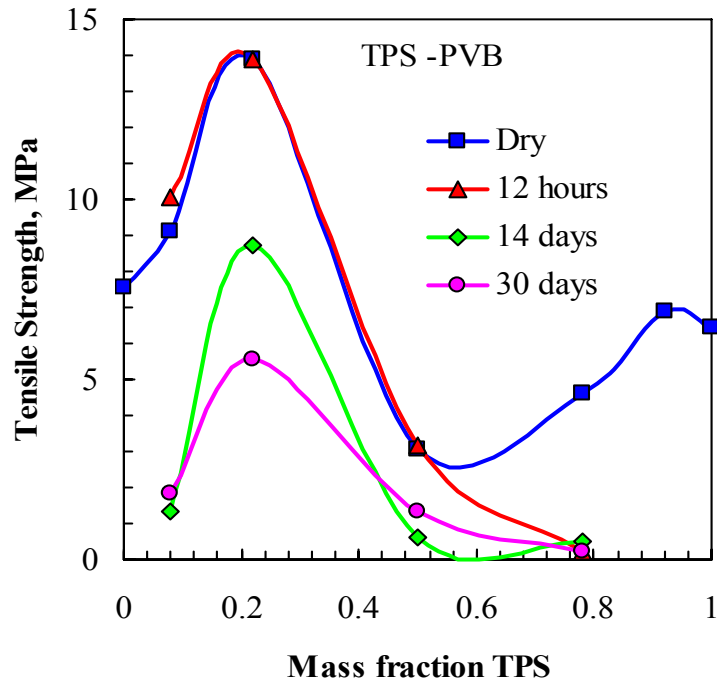


Figure 19: Effect of water soak on the tensile strength of TPS-PVB blends

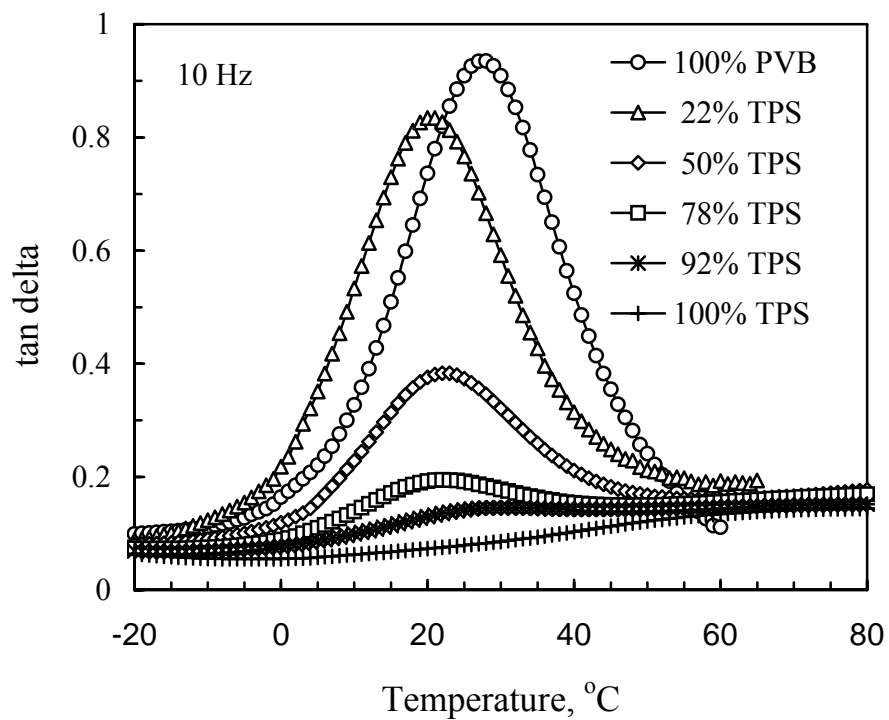


Figure 20: Tan δ (loss factor) at 10 Hz for TPS-PVB blends aged at 30 °C and 60% RH for at least 30 days

Figure 20 shows the $\tan \delta$ results obtained in the -20 to 80°C temperature window. PVB shows a strong loss peak at 28°C . TPS shows a weak loss peak below -45°C and a broad, but weak loss feature, with two peaks at higher temperatures in the DMA (not shown in Figure 20). The two high-temperature peaks are located at 94°C and 126°C respectively. Forssell *et al.* [1997] also observed low- and high-temperature loss peaks using differential scanning calorimetry (DSC) and dynamic thermal analysis (DMA) of barley starch-glycerol-water mixtures. They attributed this to phase-separation in the TPS. The system is composed of starch-rich and starch-poor regions with different glass transition temperatures (T_g 's) corresponding to these two phases.

Figure 20 reveals that the addition of TPS shifts the $\tan \delta$ peak temperature to a location that is about $5-7^\circ\text{C}$ lower than that for the neat PVB. This could indicate a degree of compatibility between the starch and PVB. However, it is more likely that the observed lowering of the T_g is the result of the PVB phase scavenging the glycerol plasticiser from the TPS. This loss peak does not shift with changing blend composition and decreases in intensity as the TPS content is increased. These observations are consistent with a two-phase nature for the TPS-PVB blends.

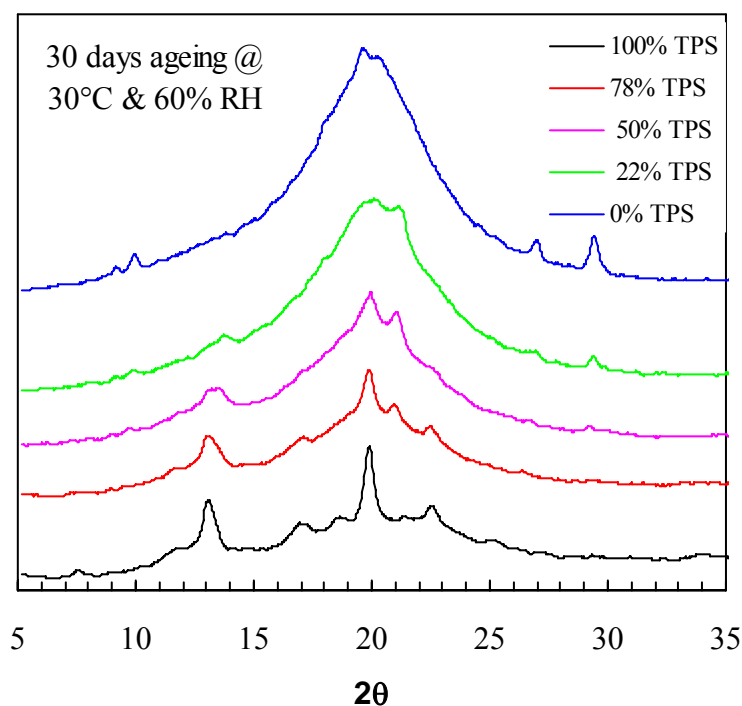


Figure 21: XRD spectra of TPS-PVB blends aged for 30 days at 30°C and 60% RH



XRD spectra of the PVB showed only a broad amorphous peak located at ca. $2\theta = 20^\circ$. The XRD spectrum of TPS features two strong, sharp peaks at $2\theta = 13^\circ$ and 20° and also some other minor peaks. These peaks do not change much in intensity during ageing. The blend with 78% TPS shows three peaks at $2\theta = 13^\circ$, 20° and 21° respectively. With ageing the first two peaks increase, whereas the third decreases in relative intensity up to the 21-day point. This indicates that the presence of PVB inhibits the crystallisation of the starch. The blend with 22% TPS still shows the lower-angle starch peak, but it is now located at $2\theta \approx 13,5^\circ$. It is likely that most of the retrogradation of the TPS observable by XRD had already occurred before the XRD spectra were obtained: It was unfortunately not possible to get immediate access to the XRD machine after the moulded samples had been prepared.

The XRD spectra are in agreement with the observations of Van Soest & Borger [1996]. The observed crystalline structure is called the V_h type and is process-induced. It results from the rapid recrystallisation of amylose in glycerol-containing TPS. The absence of B-type crystallinity shows that the granular structure of native starch was completely broken down during compounding [Van Soest & Borger, 1996]. These peaks do not change much in intensity during ageing. The blend containing 78% TPS shows exactly the same three peaks at $2\theta = 13^\circ$, 20° and 21° as the pure TPS. For the blends containing 50% TPS, the peak at $2\theta = 13^\circ$ broadens, while the other two decrease in intensity. For blends containing 78% PVB and more, there is a very broad peak at $2\theta = 20^\circ$ and the other two disappear completely. This indicates that the presence of PVB inhibits the recrystallisation of the starch.

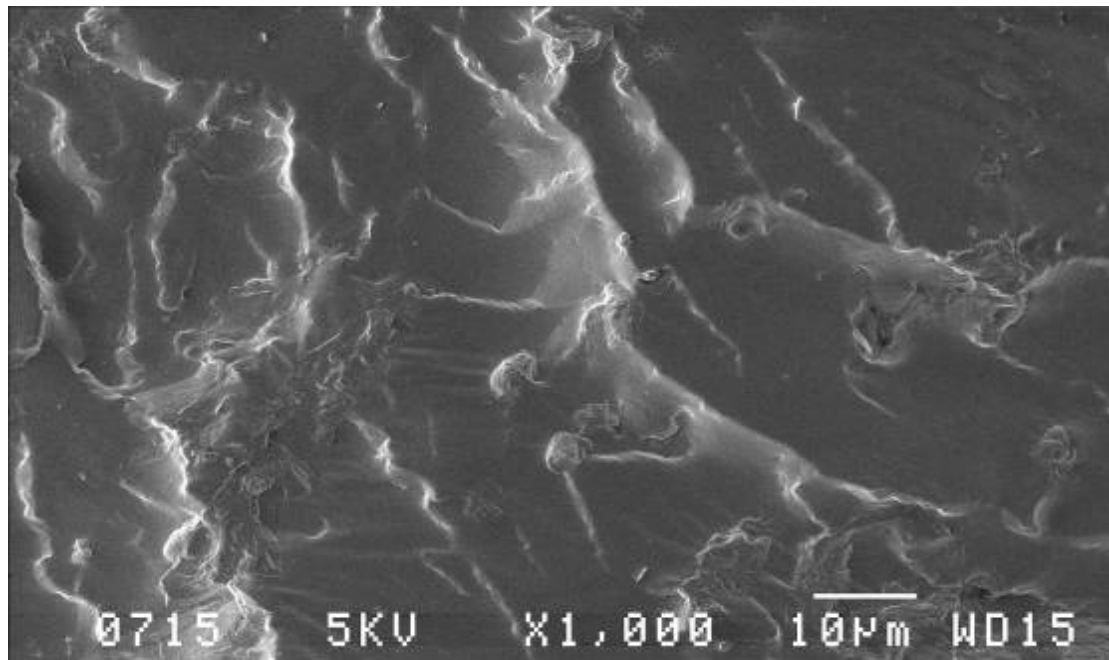


Figure 22: Scanning electron micrograph of a fracture surface of the blend containing 22% TPS

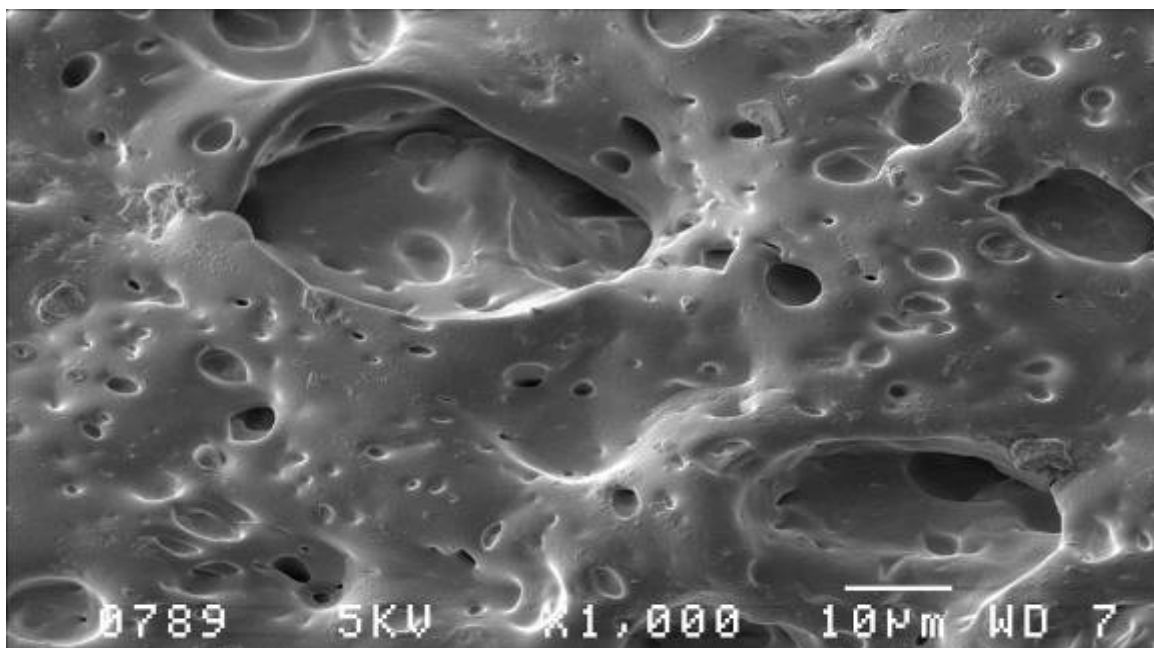


Figure 23: Scanning electron micrograph of an enzyme-eroded fracture surface of the blend containing 22% TPS

SEM studies confirmed the two-phase structure of the TPS-PVB blends. Figures 22 and 23 show fracture surfaces for the 22% TPS blend, before and after enzyme erosion. On exposure to the enzyme, the rough fracture surface develops widely distributed cavities, with sizes

ranging from ca. 1–50 μm . This suggests that the cavities result from a loss of the starch phase. The image for the 50% TPS blend appears similar, except that the cavities are more irregular in shape. As the starch content decreases, the number of cavities observed on the enzyme-eroded fracture surfaces decreases as well.

The SEM, TMA and water-resistance data all confirmed the two-phase nature of the TPS-PVB blends. This is not surprising as most polymer pairs are thermodynamically immiscible [Paul & Newman, 1978]. Phase separation leads to the creation of internal interfaces. If these have a high interfacial tension, the adhesion between the two phases will be poor. The end-result will be poor stress transfer between phases and a loss in mechanical properties [Paul & Newman, 1978]. The blends rich in PVB show improved mechanical properties, especially the compound with 22% TPS. This indicates that there is a measure of mechanical compatibility among the blends. However, similar improvement in mechanical properties was obtained merely by using gypsum as filler. Thus it is likely that, at low starch loadings, the high-stiffness starch domains simply act as dispersed particles of reinforcing filler. The high elongation-to-break values are consistent with the PVB forming the continuous phase up to 50% TPS. The lower-than-expected tensile strength of this blend can be attributed to its coarse-phase domain structure.

4.3 PVB-polyamide blends

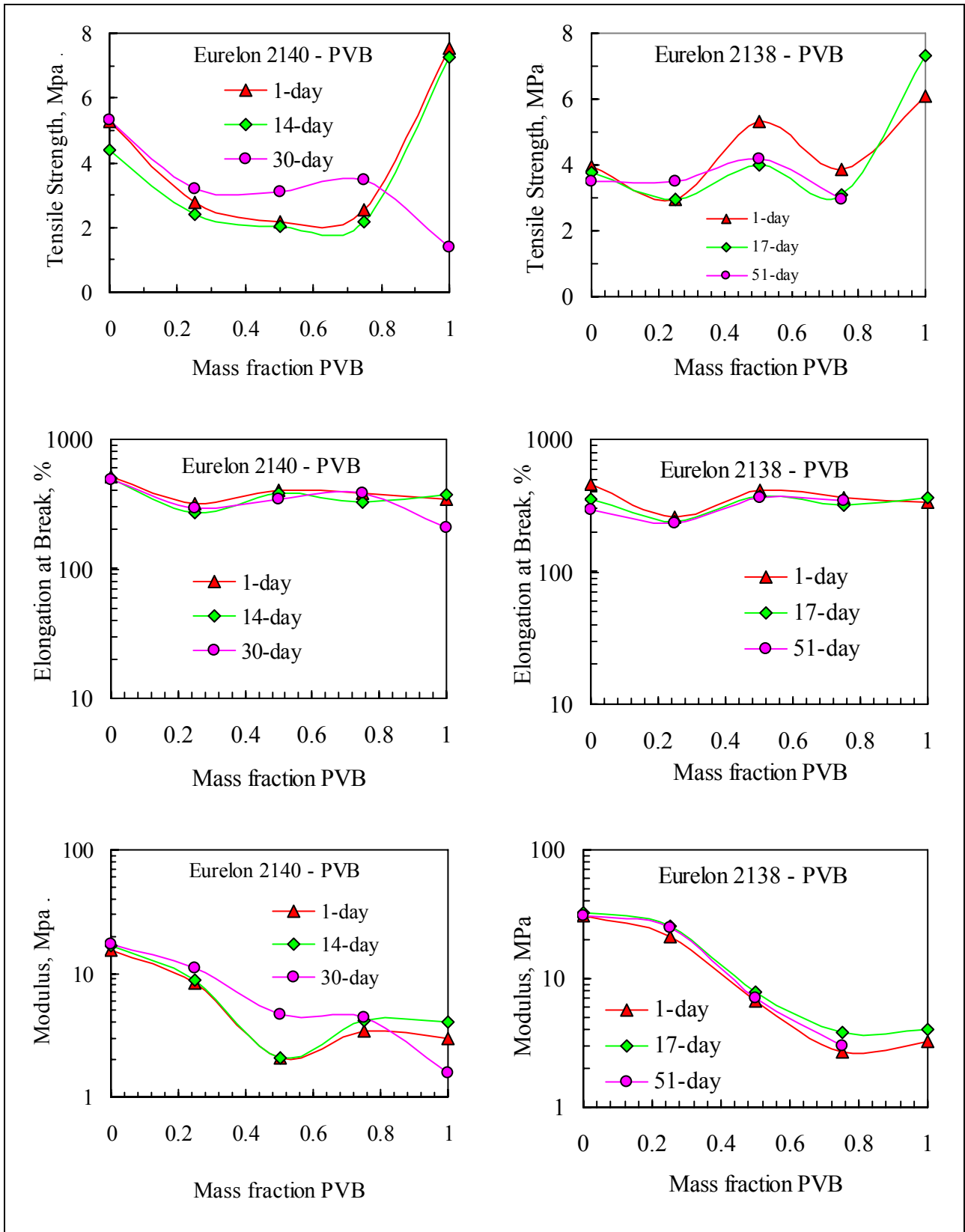


Figure 24: Effect of ageing at 30 °C and 60% RH on the mechanical properties of PVB-Euremelt blends

The mechanical properties of the Euremelt-PVB binary system are presented in Figure 24. There is scatter in the data for the effect of ageing on tensile strength for both polyamides. An initial decrease in the tensile strength is observed for the first 14 days, followed by an increase from 14 days to 30 days for both Euremelts. The modulus decreases with an increase in PVB content for both Euremelts. This is because PVB has a much lower T_g than both the Euremelts and is therefore more flexible than both the Euremelts at storage temperatures. There is no significant change in the elongation-to-break for blends containing both polyamides. This shows that the mechanical properties of these blends are not affected by ageing as are the blends containing TPS.

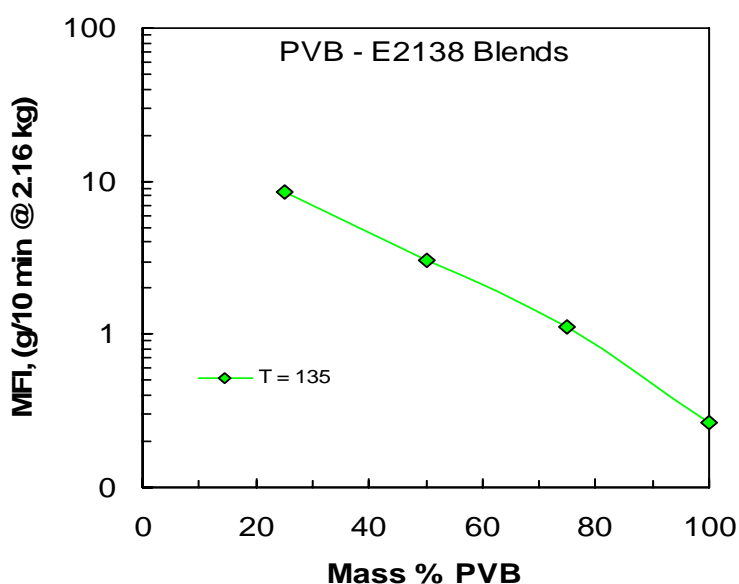


Figure 25: Effect of composition on the melt flow index (MFI) of a PVB-Euremelt blend

The melt flow index (MFI) results for the PVB-E2138 blends are presented in Figure 25. The MFI decreases with an increase in PVB content. This is because PVB behaves more like a rubber and hence is highly viscous. From the results of these experiments it was anticipated that blending PVB with polyamides would give blends with lower viscosities, which would be processable at lower temperatures and torques during extrusion, as well as allowing the injection-moulding temperatures and injection pressures to be lowered during extrusion when they were blended with TPS.



4.4 TPS-polyamide blends

The extrusion temperatures are presented in Table 12. The extrusion parameters were highly influenced by the composition of the formulation. Higher temperatures were observed for TPS-Euremelt blends with high TPS content. The reason for the lower processing temperature for blends with high Euremelt content is that the melting temperature of the Euremelts is ca. 50 °C. As a result, the extrusion parameters of the latter blends were below 100 °C, which is lower than the glass transition temperature of TPS. In these blends the TPS acted as a filler embedded in the polyamide matrix.

Table 12: Extrusion parameters for TPS-E2140 blends

| Polymer Blend | Barrel Temperature, °C | | | |
|---------------|------------------------|------------------|---------------|----------|
| | Feeding zone | Compression zone | Metering zone | Die zone |
| 100% TPS | 120 | 150 | 150 | 100 |
| 92% TPS | 110 | 140 | 140 | 100 |
| 78%TPS | 110 | 120 | 120 | 75 |
| 50% TPS | 110 | 120 | 120 | 75 |
| 22% TPS | 80 | 90 | 90 | 50 |
| 8% TPS | 80 | 90 | 90 | 50 |
| 0% TPS | 65 | 70 | 70 | 50 |

Injection moulding was a difficult process. Sticking in the sprue bush was a problem, despite the inclusion of stearyl alcohol in the formulation. “Spray and Cook” had to be sprayed into the mould after every shot. The injection pressures were lower than those of the TPS-PVB blends. As with extrusion, the injection-moulding processing parameters were influenced by the formulation of the blend. For each formulation the optimum settings were those that enabled the mould to be filled 100% without warpage and flashing. The injection-moulding parameters for the TPS-Euremelt blends are given in Table 13.



Table 13: Injection moulding parameters for TPS-Euremelt [E2140 and E2138] blends

| Polymer Blend | Barrel Temperature, °C | Injection Pressure, bar |
|----------------------|-------------------------------|--------------------------------|
| 100% TPS | 140; 145; 145; 150 | |
| 92% TPS | 140; 140; 140; 130 | |
| 78%TPS | 140; 140; 140; 130 | |
| 50% TPS | 100; 105; 110; 100 | 80 |
| 22% TPS | 90; 90; 90; 90 | (all compositions) |
| 8% TPS | 90; 90; 90; 90 | |
| 0% TPS | 90; 90; 90; 90 | |

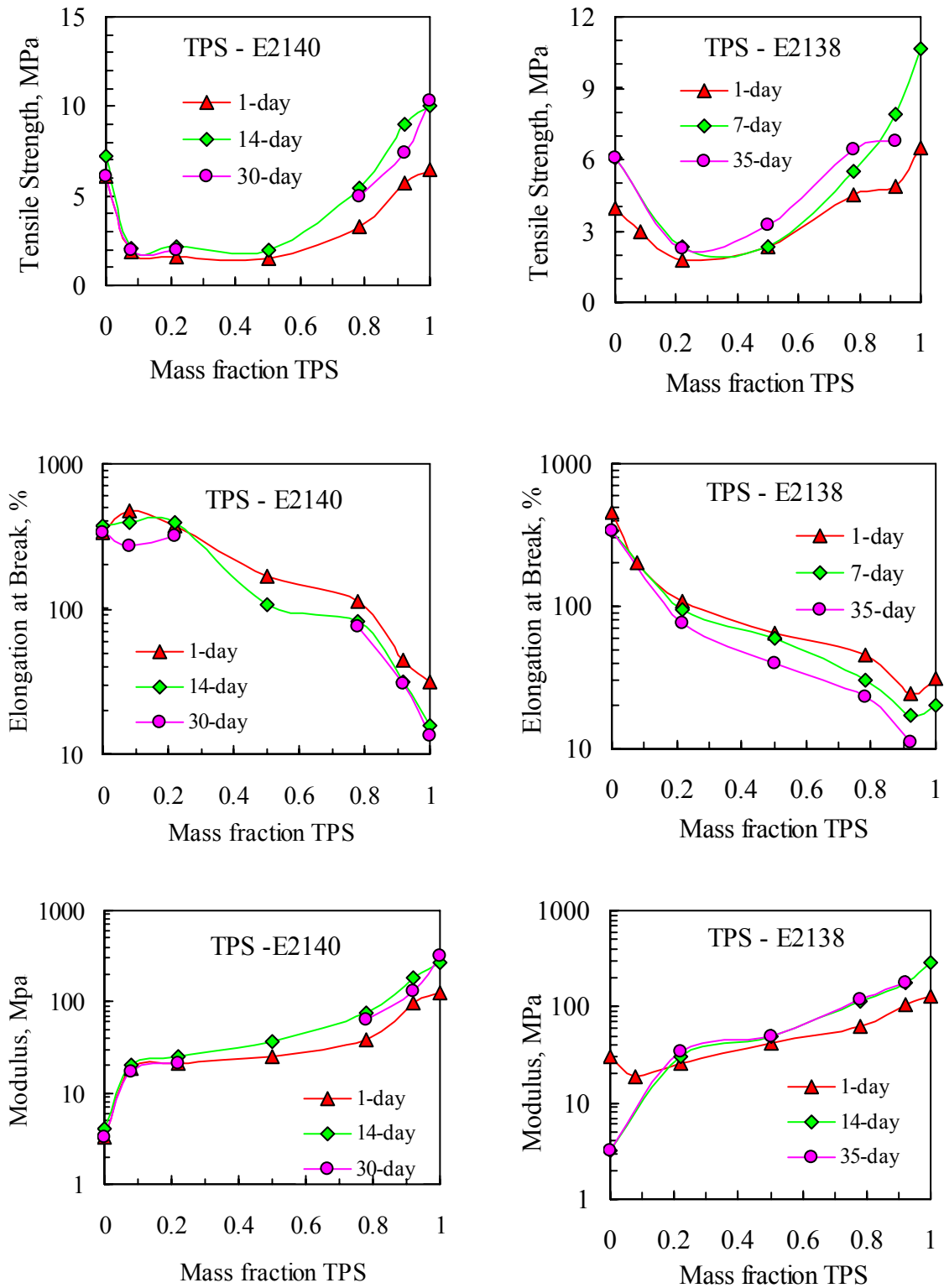


Figure 26: Effect of ageing at 30 °C and 60% RH on the mechanical properties of TPS-polyamide blends

The mechanical properties for the TPS-polyamide binary system are illustrated in Figure 26.

For blends containing more than 22% polyamide, there is a general increase in tensile strength and the Young's modulus increases with an increase in ageing time, while the elongation-to-break decreases. This is true for blends of both Eurelon 2140 and Eurelon 2138 and is due to retrogradation. Retrogradation is the change in properties of thermoplastic starch-based materials with time, in this case caused by the recrystallisation of amylose and amylopectin during ageing. Materials with a high TPS content are very brittle, while materials with a high polyamide content are tough and strong for both the E2140 and E2138 blends. For blends containing E2140, the numerical values for the tensile properties after 14 days of ageing are very close, in some instances equal, to the values after 30 days of ageing. This means that the degree of recrystallisation is very low between 14 and 30 days of ageing.

There is a general decrease in tensile strength for blends containing up to 78% polyamide. This is because the melting temperature for TPS is ≈ 144 °C and these blends were processed well below this temperature (refer to Table 12). The starch granules did not melt-mix with the polyamides at these concentrations and therefore acted like flaws. This resulted in the decrease in tensile strength compared with the pure components. This phenomenon is, however, not very visible on the SEM micrograph for the blends containing 92% Euremelts as presented in Figures 27 and 28.

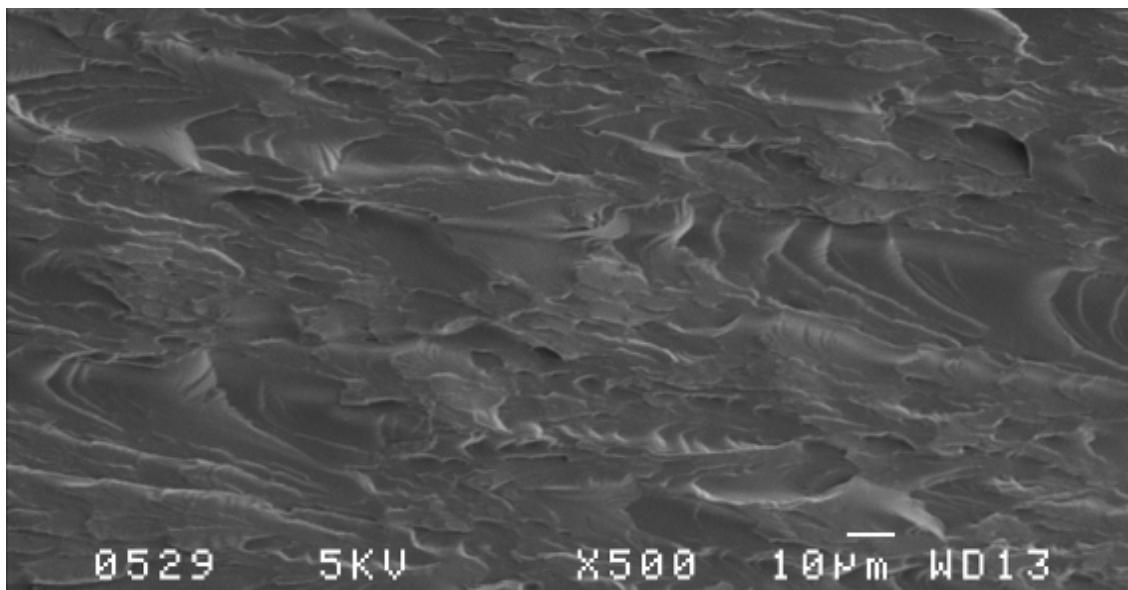


Figure 27: Scanning electron micrograph of a fracture surface of the blend containing 92% E2138

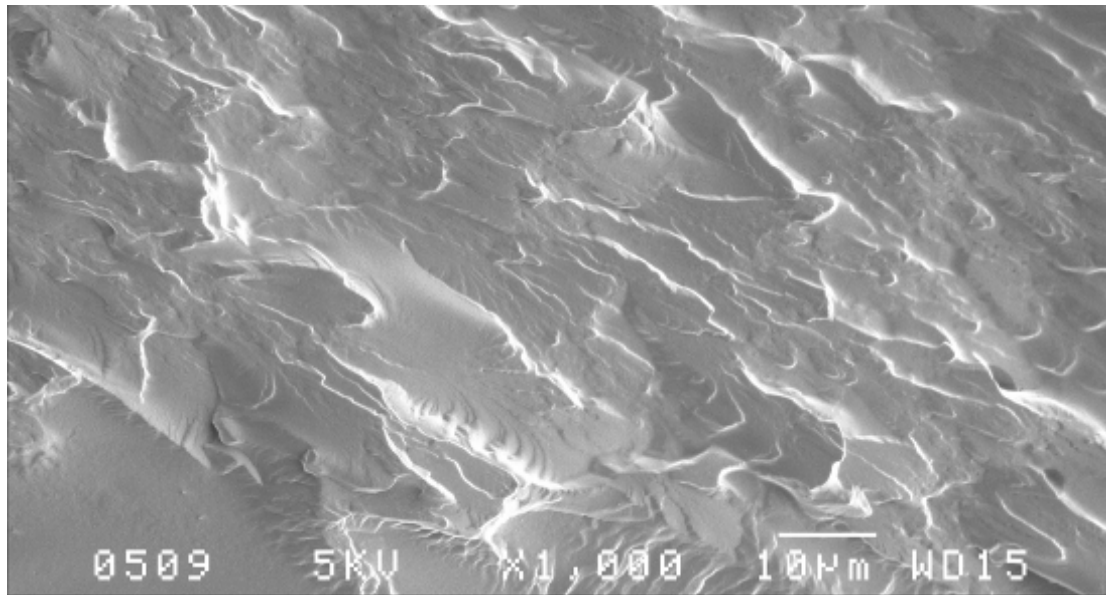


Figure 28: Scanning electron micrograph of a fracture surface of the blend containing 92% E2140

More information can be interpreted from Figures 29 and 30, which show optical micrographs of the blends containing 92% E2138 and E2140. In these micrographs the starch behaves as a particulate filler in a continuous phase of both polyamides. The dark particles in the micrographs are chunks of TPS that were broken down by shear forces during extrusion. These particles act like flaws in the polyamide, resulting in a decrease in tensile strength.

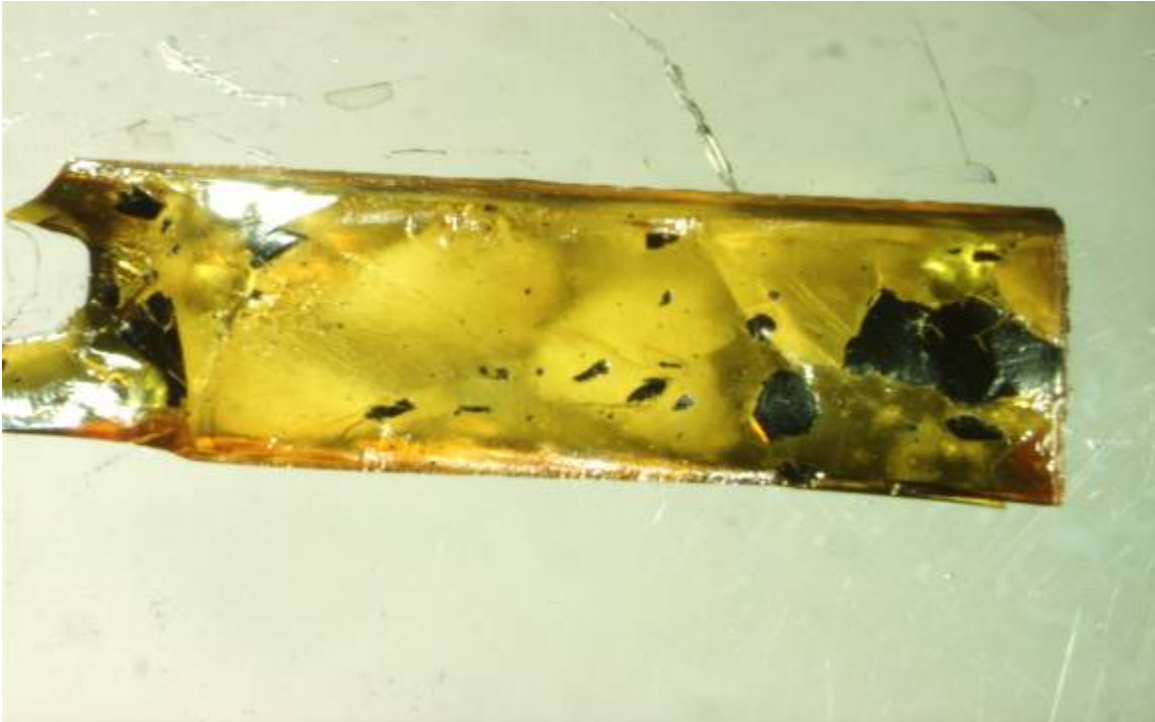


Figure29: Optical micrograph of a fracture surface of the blend containing 92% E2138

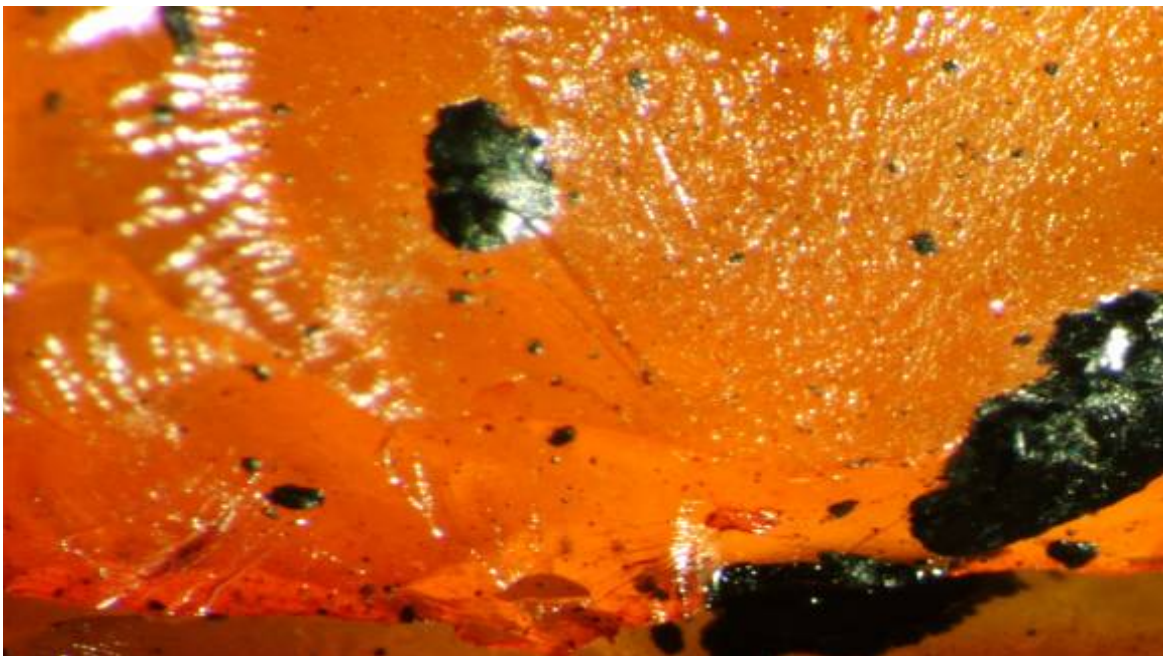


Figure 30: Optical micrograph of a fracture surface of the blend containing 92% E2140

Figure 31 illustrates the effect of water soak on the mechanical properties of the TPS-Euremelt 2140 blends. The blend containing 50% E2140 shows the best water resistance. These values decrease with ageing time. Blends containing more than 50% polyamide lasted for the first seven days, while pure TPS did not last even for a day.

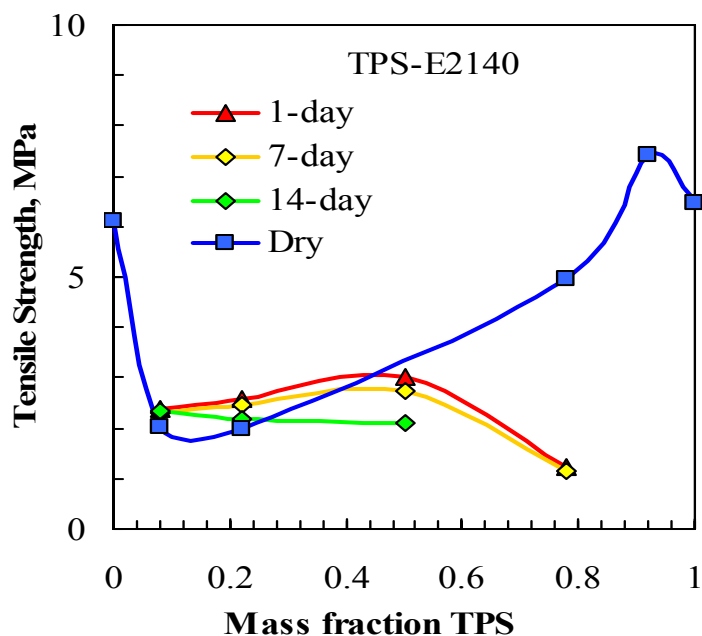


Figure 31: Effect of water soak on the tensile strength of TPS-E2140 blends

All the X-ray diffraction micrographs for TPS-Euremelt blends are contained in Appendix A. The micrographs for the pure compounds and all the formulations after 30 days of ageing are presented in Figure 32. For both the pure polyamides there is a broad peak at $2\theta = 20^\circ$, showing that they are both amorphous polymers. Blends containing 50% and more of TPS have two sharp peaks: a higher-intensity one at $2\theta = 20^\circ$ and a smaller one at $2\theta = 13.5^\circ$. With decreasing TPS content, the intensity of both peaks decreases. For blends containing 92% polyamide, a small bump can be seen at $2\theta = 13.5^\circ$ and a broad peak at $2\theta = 20^\circ$.

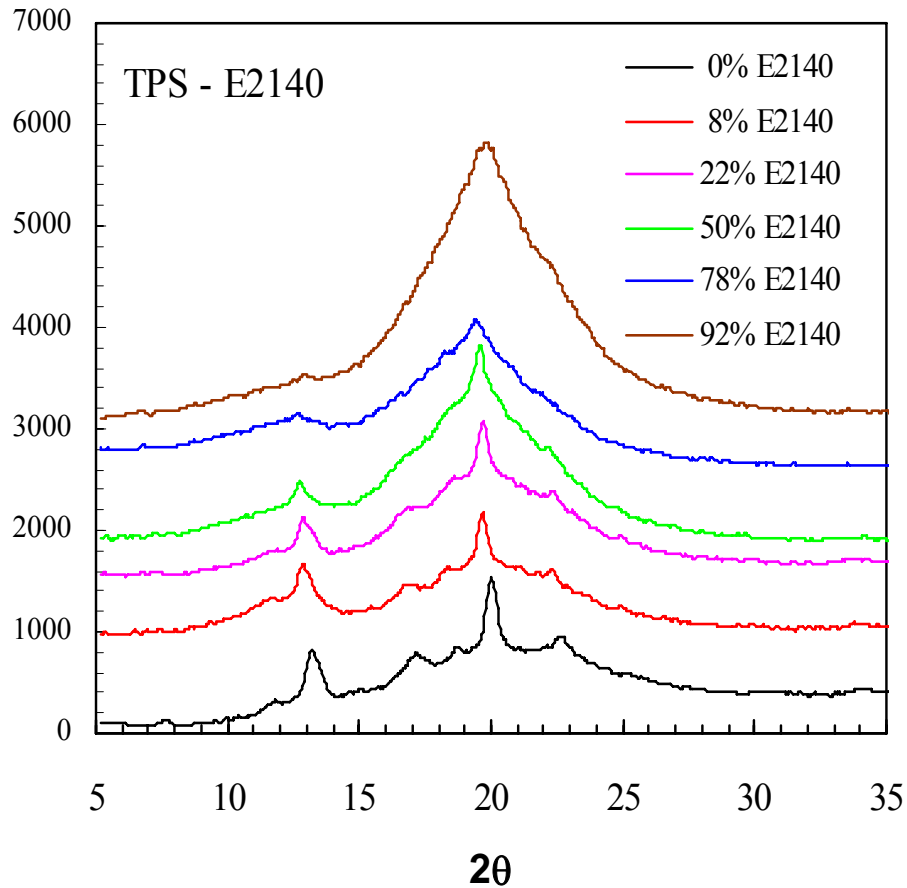


Figure 32: XRD spectra of TPS-E2140 blends aged for 30 days at 30 °C and 60% RH

The effect of ageing at 30 °C and 60% RH on the mechanical properties of the TPS-EMS blends is different from that observed for the Euremelt hot-melt-adhesive polyamides. These trends are illustrated in Figure 33. Tensile strength and elongation-to-break decrease with an increase in TPS content, while the Young's modulus remains unchanged. There are no significant changes in the mechanical properties with ageing. TPS is compatible with EMS and results in single-phased blends. The fact that there are no changes in the mechanical properties with ageing shows that EMS effectively retards retrogradation of thermoplastic starch [Beuhler *et al.*, 1994].

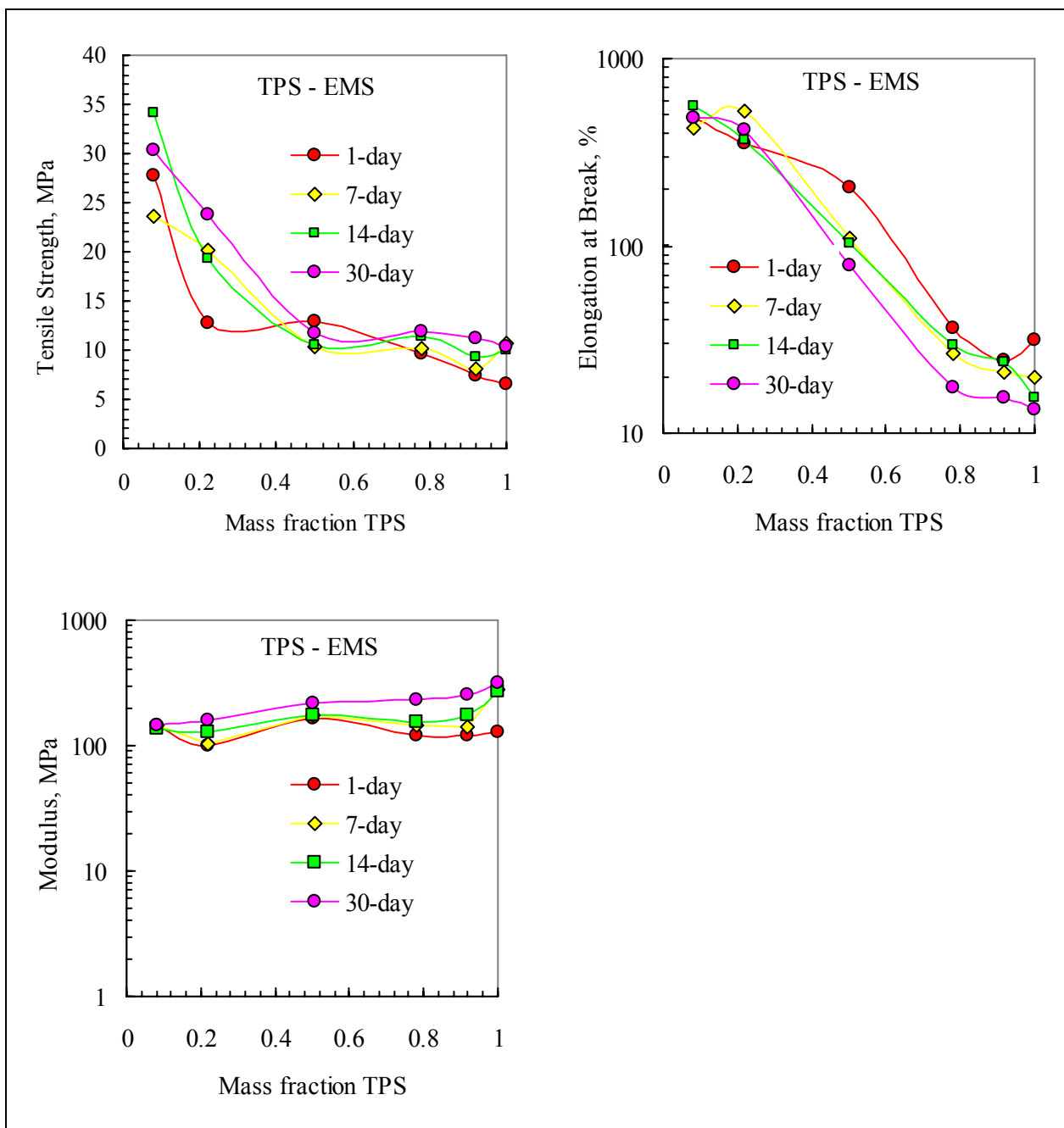


Figure 33: Effect of ageing at 30 °C and 60% RH on the mechanical properties of TPS-EMS polyamide blends

4.5 TPS-PVB-polyamide systems

The processing parameters of TPS-PVB-polyamide blends are given in Table 14. The extrusion parameters of these blends are lower than those of TPS-PVB blends and slightly above those of TPS-E2140 blends. This is in agreement with the MFI results for the PVB-

polyamide blends discussed in Section 4.3. With an increase in the PVB content, the MFI decreased. This suggests that blending PVB with E2140 results in blends with lower viscosities and hence the decrease in the processing temperatures required for the TPS-PVB-E2140 blends.

Table 14: Extrusion parameters for TPS-PVB-E2140 blends

| Polymer Blend | Barrel Temperature, °C | | | |
|---------------|------------------------|------------------|---------------|----------|
| | Feeding zone | Compression zone | Metering zone | Die zone |
| TPS 6 | 115 | 120 | 120 | 70 |
| Eu 10 | 115 | 120 | 120 | 70 |
| Eu 12 | 115 | 120 | 120 | 70 |
| Eu 11 | 115 | 120 | 120 | 70 |
| Eu 9 | 115 | 120 | 120 | 70 |

The injection-moulding parameters for the TPS-PVB-E2140 blends are given in Table 15. The injection-moulding temperatures decrease with a decrease in TPS content in the formulation.

Table 15: Injection moulding parameters for TPS-PVB-E2140 blends

| Polymer Blend | Blend Composition, mass % | | | Barrel Temperature, °C | Injection Pressure, bar |
|---------------|---------------------------|------|-------|------------------------|-------------------------|
| | TPS | PVB | E2140 | | |
| TPS 6 | 100 | 0 | 0 | 140; 145; 145; 150 | 70 |
| Eu 10 | 66.8 | 16.6 | 16.6 | 135; 120; 120, 110 | 80 |
| Eu 12 | 33.3 | 33.3 | 33.3 | 105; 115; 110, 100 | 80 |
| Eu 11 | 16.6 | 16.6 | 66.8 | 105; 115; 110;100 | 80 |
| Eu 9 | 16.5 | 66.8 | 16.6 | 110; 115; 110; 100 | 80 |

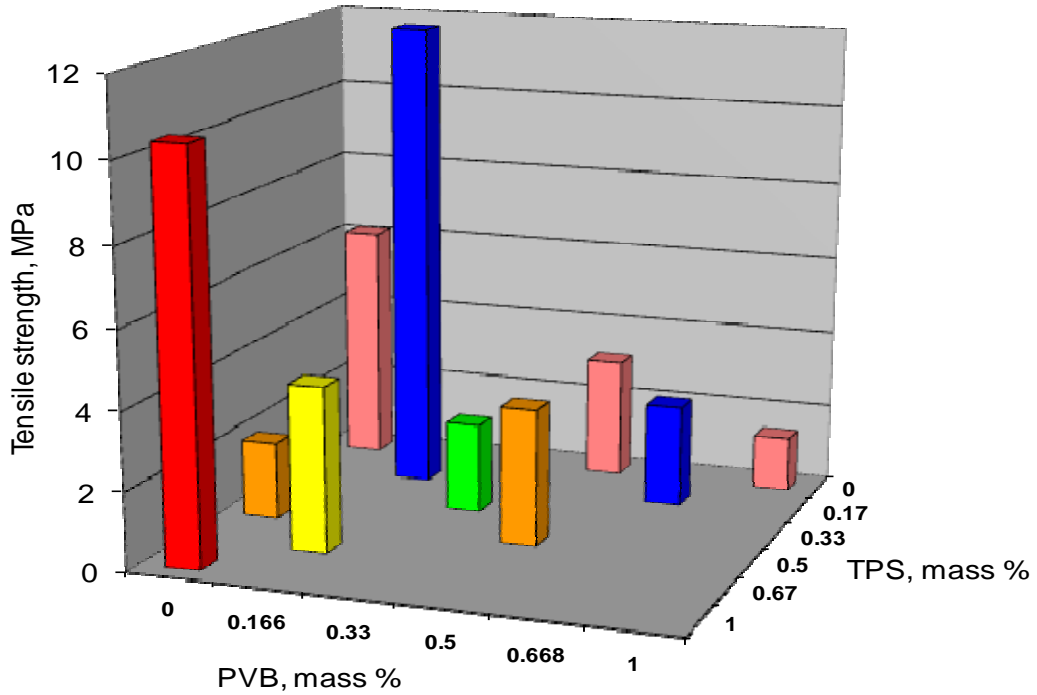


Figure 34: Effect of ageing at 30 °C and 60% RH on the tensile stress of TPS-PVB-polyamide (E2140)

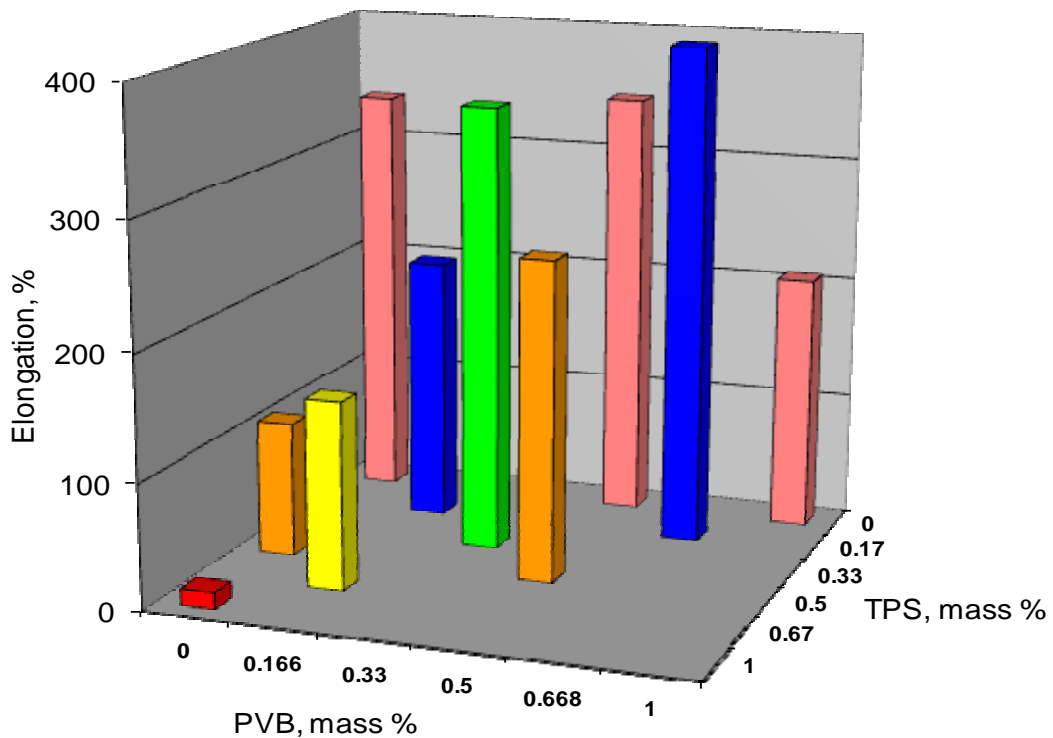


Figure 35: Effect of ageing at 30 °C and 60% RH on the elongation-to-break of TPS-PVB-polyamide (E2140)

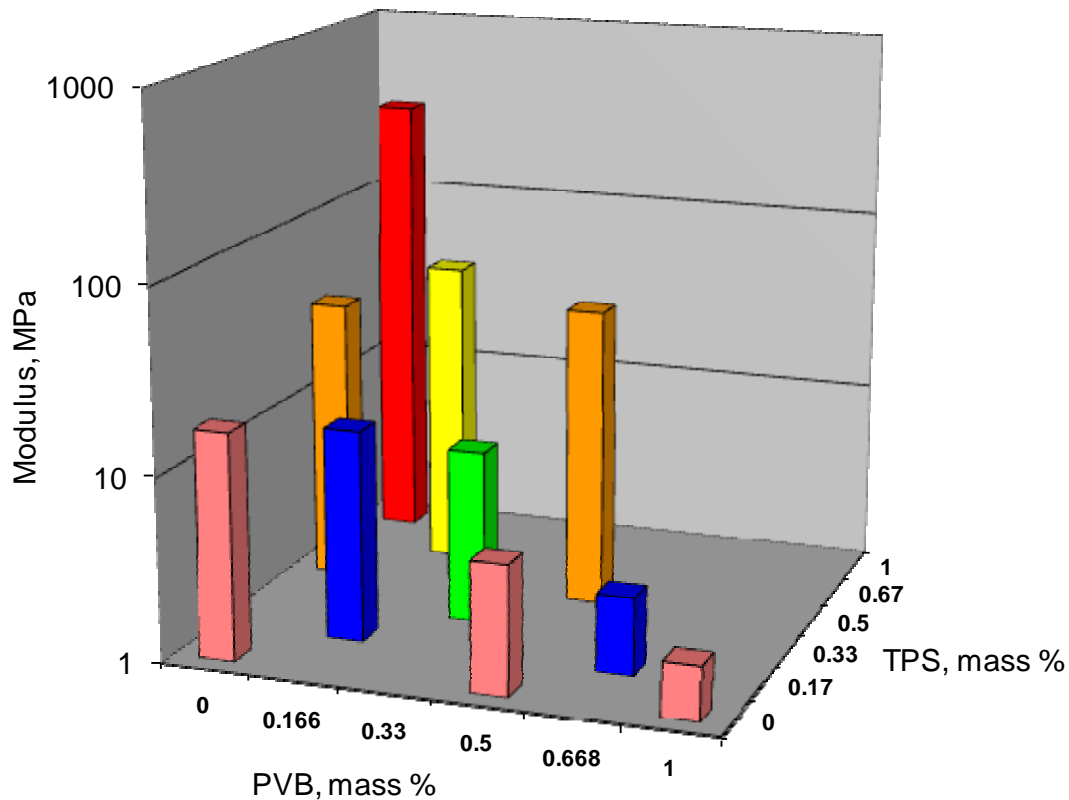


Figure 36: Effect of ageing at 30 °C and 60% RH on the modulus of TPS-PVB–polyamide (E2140)

The effect of ageing on the mechanical properties of TPS-PVB-polyamide (E2140) blends is presented in Figures 34 to 36. Tensile strength and modulus increase with an increase in TPS content, while elongation-to-break decreases. This is due to retrogradation. A slight increase was observed for the tensile strength and modulus over the first 14 days and thereafter no further changes in mechanical properties were observed. However, the ageing process was only monitored for a period of 30 days and further changes may be possible after longer periods of ageing.

4.6 TPS–PVB-anhydride systems

In order to incorporate more than 8% filler content into TPS-PVB blends, PVB was pre-compounded with PVB. This is because of (a) the effect that fillers have in increasing the



effective viscosity of a suspension, and (b) the reduction in water and in the availability of plasticiser for gelatinisation owing to occlusion inside agglomerates of filler particles. This led to slow gelatinisation, forming a thermoplastic starch that was only slightly plasticised, resulting in high viscosities. High torque was therefore required to mix it with the filler. Only formulations containing less than 8% filler could be extruded with TPS.

The anhydride (“dead burned” calcium sulphate) was used as a filler for PVB. A 50%-filled (by mass) PVB compound was first prepared using the twin-screw extruder. Thereafter, this compound was melt-mixed with TPS by extrusion using the single-screw extruder, resulting in TPS-PVB-anhydride polymer blends. Up to 25% anhydride compound could be melt-mixed with TPS. The extrusion parameters for the TPS-PVB-anhydride blends are given in Table 16 and the injection-moulding parameters in Table 17.

Table 16: Extrusion parameters for TPS-PVB-anhydride blends

| Polymer Blend | Barrel Temperature, °C | | | |
|---------------|------------------------|------------------|---------------|-----|
| | Feeding zone | Compression zone | Metering zone | Die |
| TPS 9 | 120 | 150 | 148 | 100 |
| TPS 10 | 120 | 150 | 145 | 90 |
| TPS 11 | 110 | 135 | 130 | 80 |
| TPS 12 | 120 | 150 | 150 | 90 |
| TPS 13 | 120 | 150 | 150 | 100 |

Table 17: Injection moulding parameters for TPS-PVB-anhydride blends

| Polymer Blend | Blend Composition, mass % | | | Barrel Temperature, °C | Injection Pressure, bar |
|---------------|---------------------------|-----|-----------|------------------------|-------------------------|
| | TPS | PVB | Anhydride | | |
| TPS 10 | 78 | 11 | 11 | 150; 140; 135; 130 | 70 |
| TPS 9 | 50 | 25 | 25 | | 82 |
| TPS 12 | 39 | 38 | 25 | | 82 |
| TPS 11 | 25 | 50 | 25 | | 82 |
| TPS 13 | 11 | 64 | 25 | | 105 |

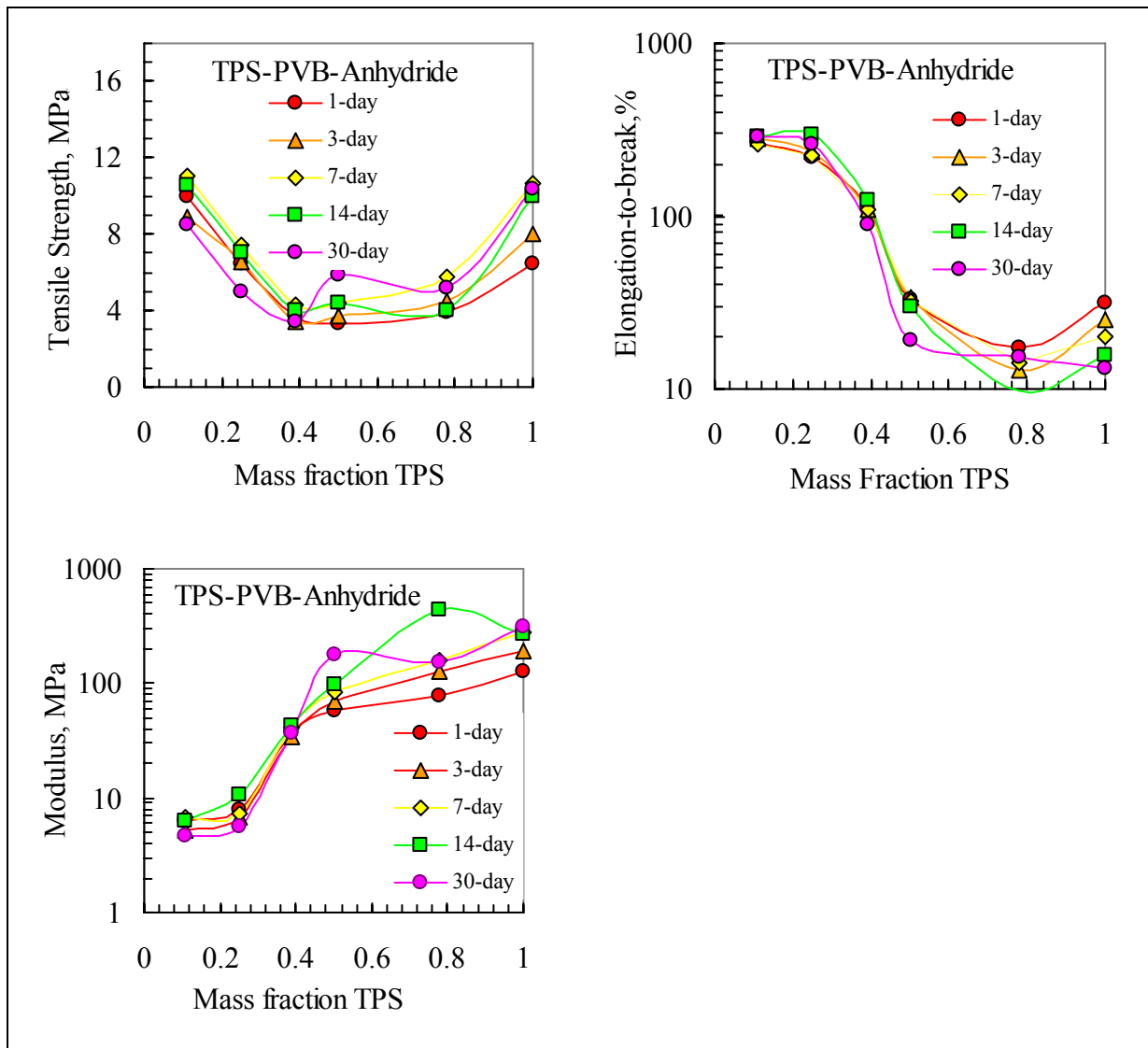


Figure 37: Effect of ageing at 30 °C and 60% RH on the mechanical properties of TPS-PVB-anhydride blends

The effect of ageing on the mechanical properties of TPS-PVB-anhydride blends is presented in Figure 37. There is a decrease in elongation-to-break with an increase in TPS content, while the modulus increases. There is a general decrease in the tensile strength for blends containing 25% by mass of anhydride, and a slight increase is noted for the blend containing 78% TPS and equal amounts of PVB and anhydride. This trend is independent of the anhydride content since its concentration is kept constant at 25% by mass. This phenomenon cannot be explained by retrogradation. It is more likely that the TPS acts as a filler in this blend, hence the observed decrease in elongation-to-break and the increase in the modulus.

5 CONCLUSIONS

The extrusion trials done using the Berstorff twin-screw extruder and the Rapra single-screw extruder illustrate that the conversion of granular starch into thermoplastic starch requires gradual application of shear in the presence of high plasticiser contents. Excessive shear is harmful to the starch and results in embrittlement due to a reduction in the average molar mass. Every extruder is unique and therefore processing parameters, barrel temperatures, screw speeds, etc. should be set up by systematic experimentation.

Initial extrusion and moulding trials revealed that the TPS compounds were very difficult to process. Difficulties were encountered with feeding the dry blends into the compounding extruder. The addition of 2,5% precipitated silica was necessary to facilitate feeding of the dry blends into compounding extruder.

The compounding processing window is relatively small. Only formulations within a narrow range of water and glycerol content were extrudable. All TPS compounds showed poor processability during injection moulding, especially in the sprue part. This was improved by adding stearyl alcohol at ca. 1,5% as an external lubricant and mould-release agent. Nevertheless, for some compositions it was also necessary to use “Spray-and-Cook” as mould-release agent during injection moulding.

Good mechanical properties were only achieved by using high-amylose starch. Starch high in amylopectin was very difficult to process and showed excessive retrogradation, with samples even cracking spontaneously during ageing. Increasing the glycerol content increased the elongation-to-break but reduced the tensile strength of TPS compounds.

The TPS-PVB blends showed highly non-linear composition-dependence. Scanning electron microscopy (SEM) and dynamic mechanical analysis (DMA) revealed a phase-separated nature for all the TPS-PVB blend compositions investigated. The tensile properties were negatively affected by ageing in a high-humidity environment and they deteriorated rapidly when the samples were soaked in water. Synergistic property enhancement was observed for a compound containing 22% thermoplastic starch. It featured a higher tensile strength, showed better water resistance and was significantly less affected by ageing. At higher PVB levels, the property dropped to values that were lower than expected from the linear blending rule.



Blending the TPS with polyamides improved the processability and also the mechanical properties. Blends with polyamide EMS were found to have reasonably good mechanical properties. However, starch at low levels did not provide the polyamides with a reinforcing effect. The phase separation during extrusion was caused by the difference in glass transition temperatures, resulting in poor tensile properties for blends containing more than 50% Euremelt. The properties of all the compounds investigated were affected by moisture content and also by ageing.

Blends with recycled plasticised PVB showed highly non-linear mechanical property variations with composition. The best was a compound containing approximately 22% TPS. However, DMA, enzyme erosion and SEM experiments showed that all the TPS-PVB blends had a phase-separated morphology. It is concluded that, at low to medium starch content, the starch acts as reinforcing filler in the PVB matrix. The deterioration in mechanical properties at higher starch levels is attributed to the starch becoming the continuous phase.

The two-phase nature of the TPS-PVB blends is not surprising as most polymer pairs are thermodynamically immiscible [Paul and Newman, 1978]. This phase separation leads to the creation of internal interfaces. If these have a high interfacial tension, there will be poor adhesion between the two phases. The end-result is poor stress transfer between phases and a loss in mechanical properties, as observed in the present case for the blends with high TPS content [Paul and Newman, 1978].

The blends rich in PVB show better mechanical properties, especially the compound with 22% TPS. Although this blend is also phase-separated, there appears to be sufficient interaction between the polymer pairs at the molecular level to induce mechanical “compatibility”, rather than miscibility. For this blend the stiffer starch domains appear to provide some reinforcing effect, leading to an increase in the tensile strength and modulus. Furthermore, the SEM evidence suggests that debonding at the interfaces occurs only after some plastic deformation of the matrix has occurred. This internal energy-absorption process explains the increase in the measured elongation-to-break for this sample.



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APPENDICES

APPENDIX A: X-RAY DIFFRACTION SPECTRA

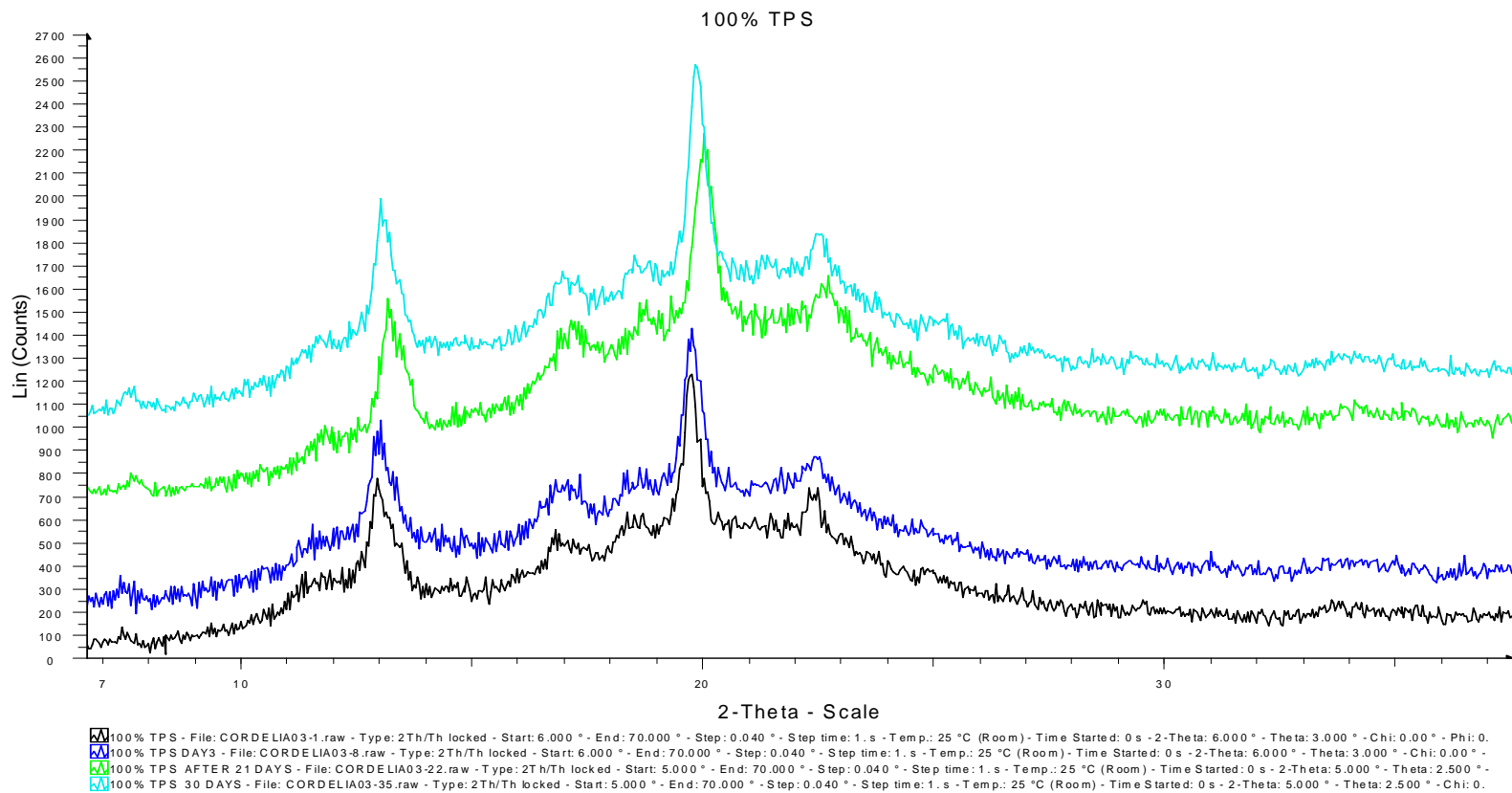


Figure A1: XRD spectra of the TPS-PVB blend containing 0% PVB blends at 30 °C and 60% RH

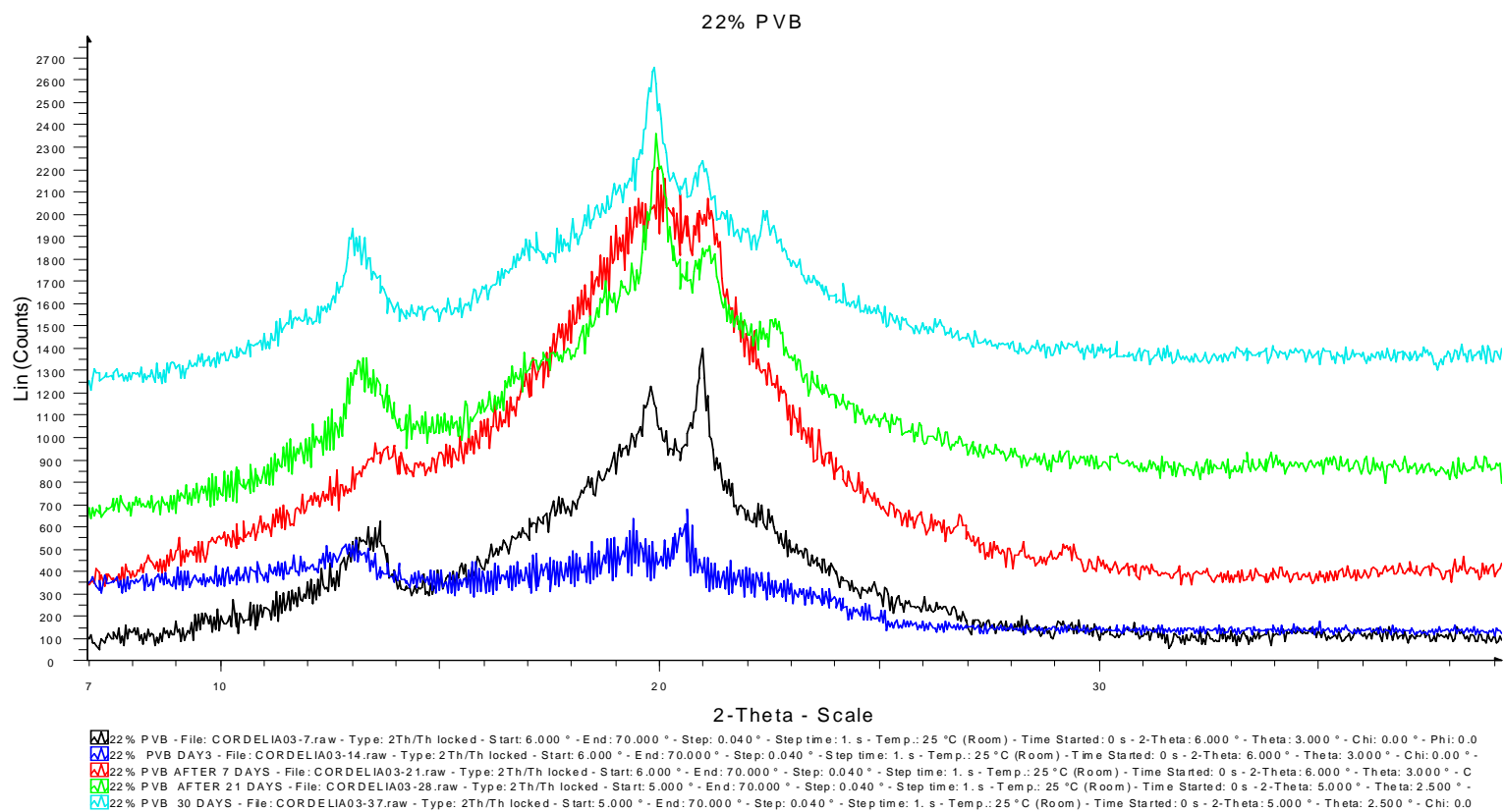


Figure A2: XRD spectra of the TPS-PVB blend containing 22% PVB blends at 30 °C and 60% RH

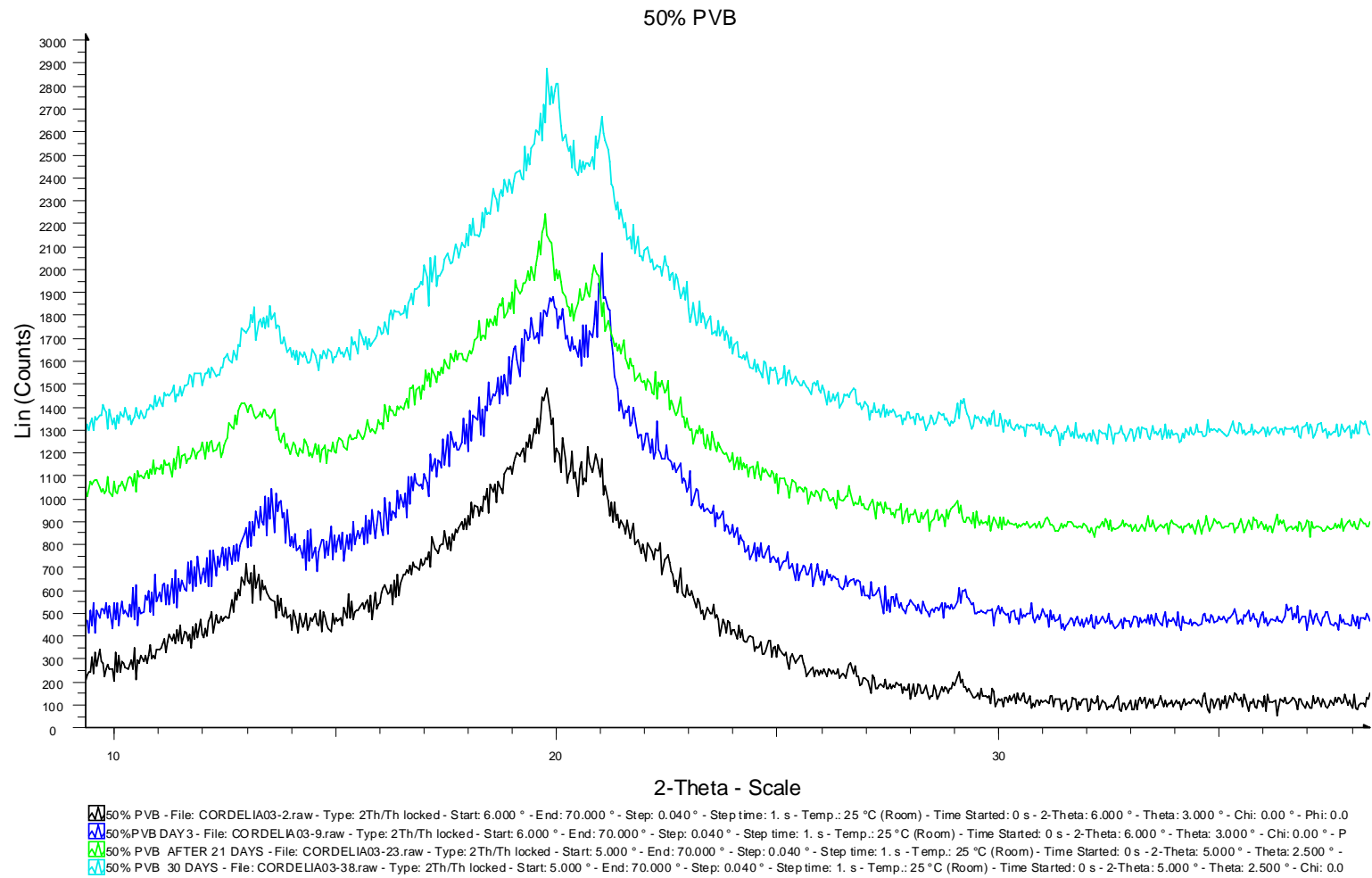


Figure A3: XRD spectra of the TPS-PVB blend containing 50% PVB blends at 30 °C and 60% RH

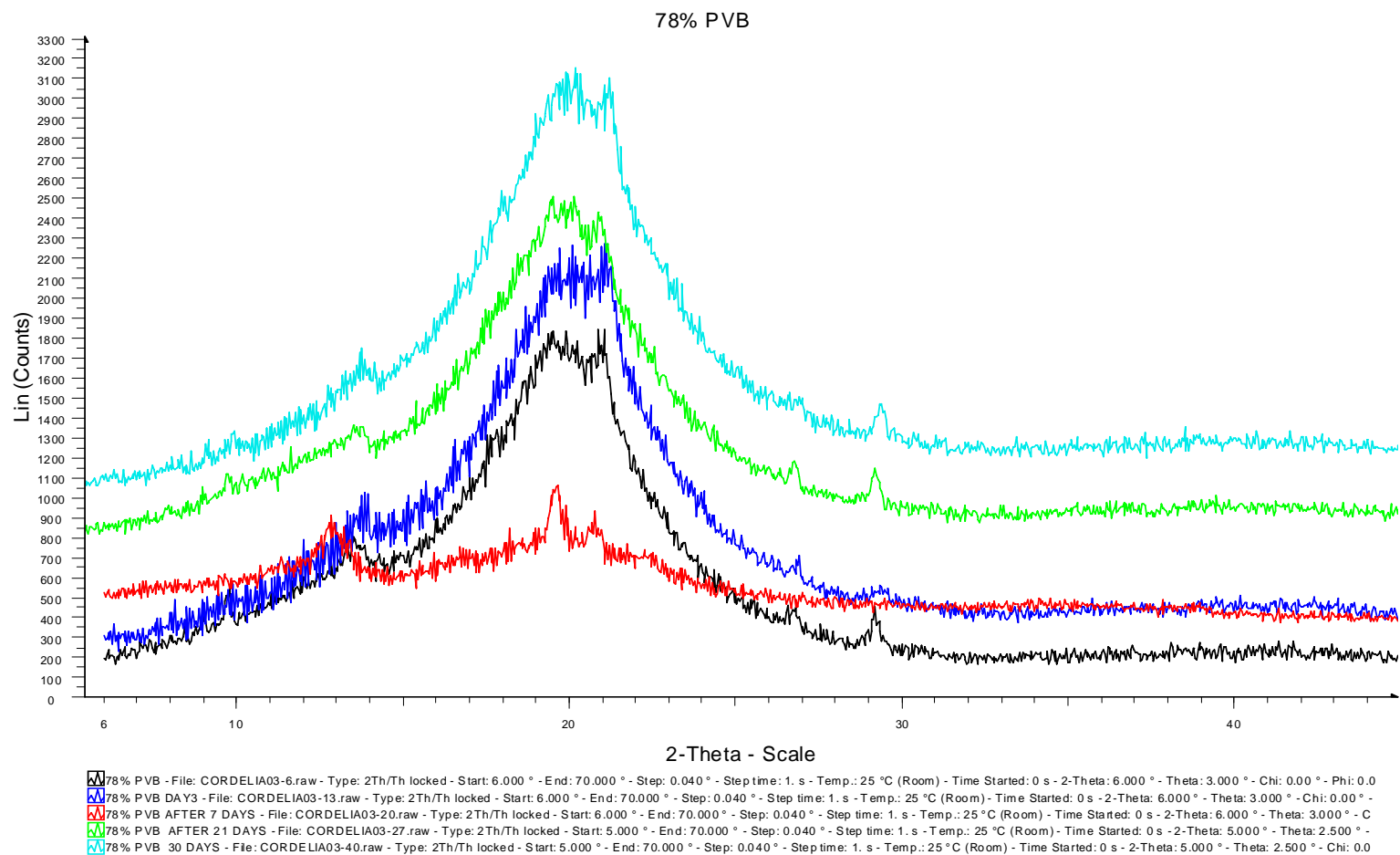


Figure A4: XRD spectra of the TPS-PVB blend containing 75% PVB blends at 30 °C and 60% RH

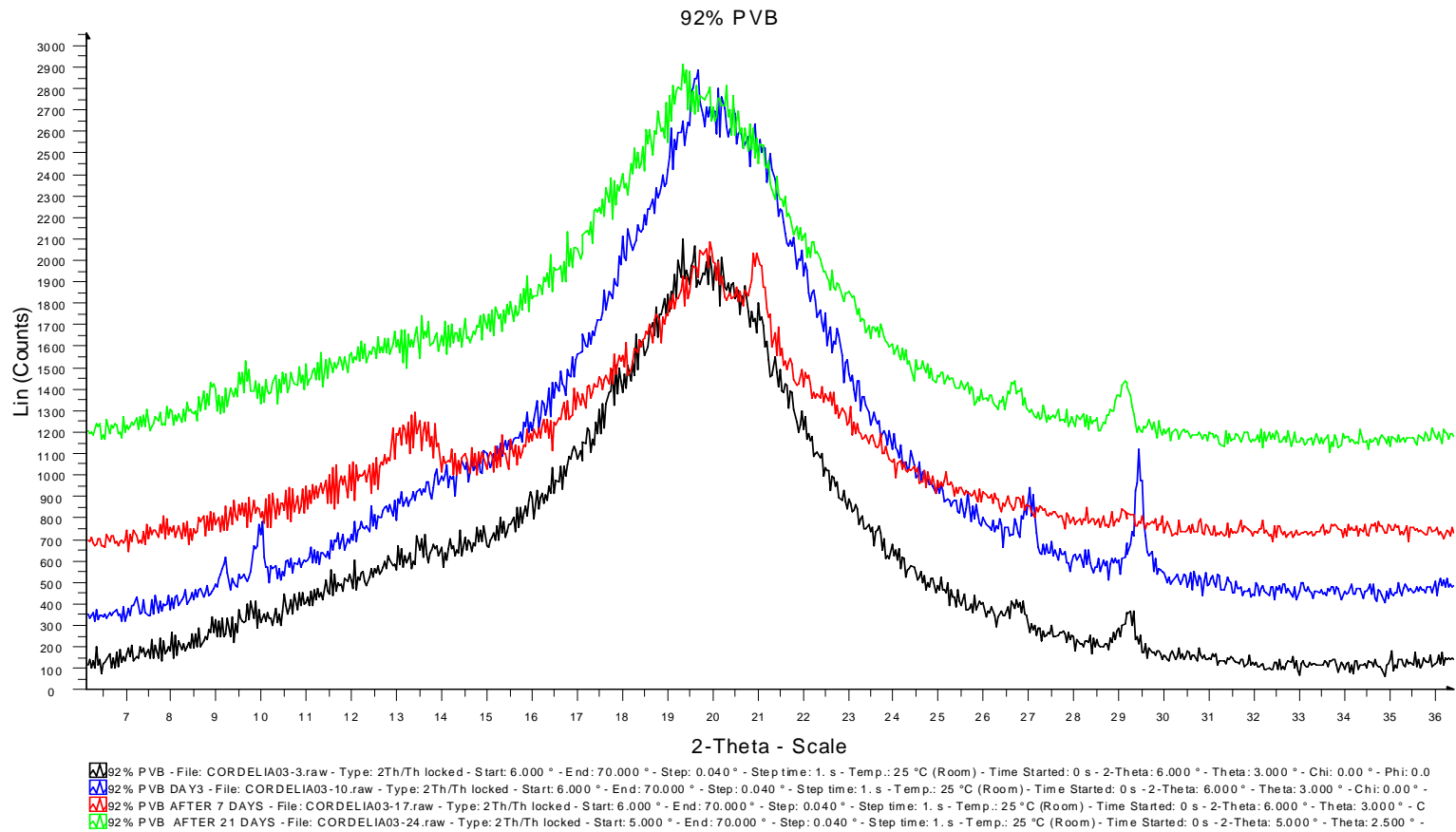


Figure A5: XRD spectra of the TPS-PVB blend containing 92% PVB blends at 30 °C and 60% RH

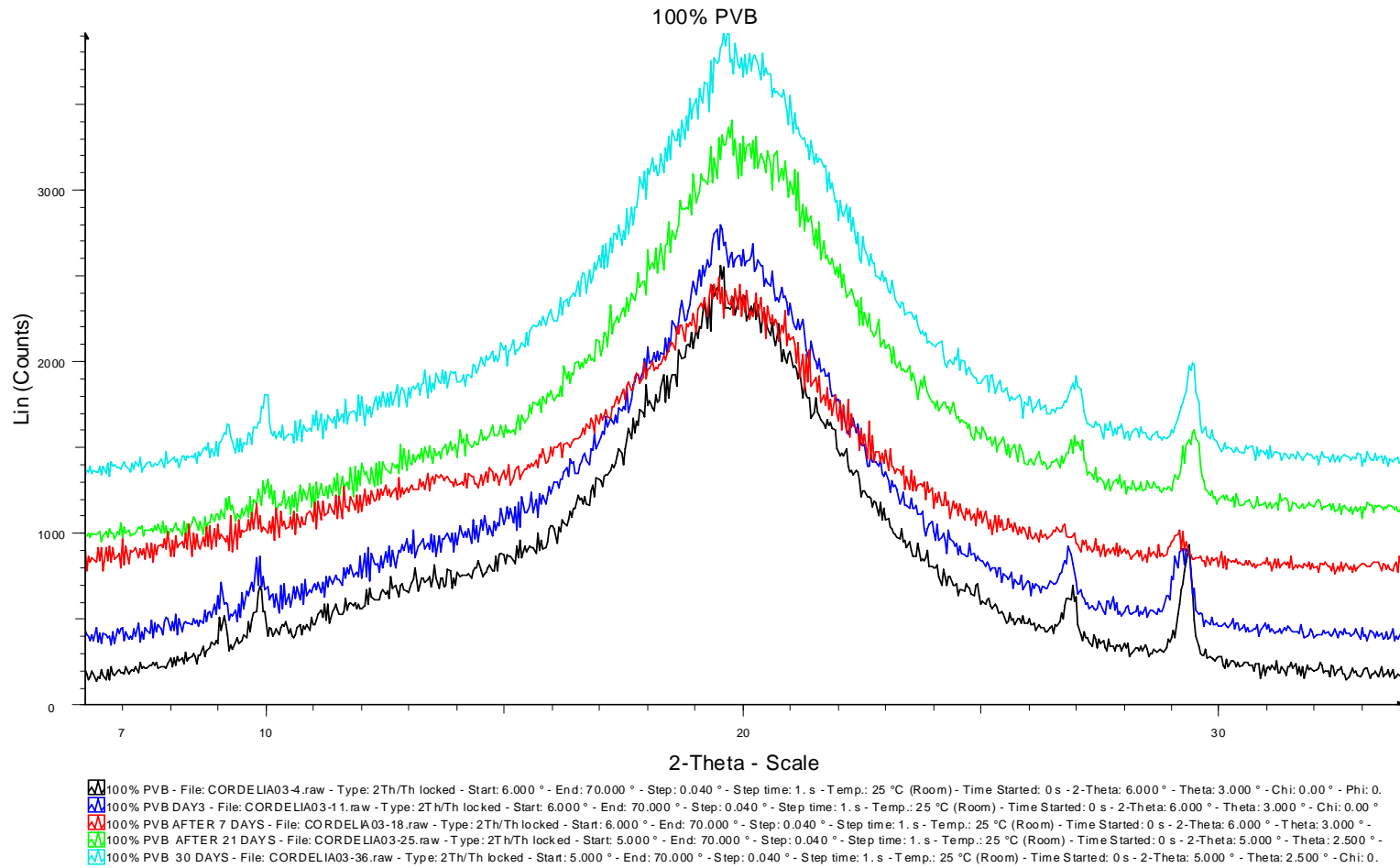


Figure A6: XRD spectra of the TPS-PVB blend containing 100% PVB blends at 30 °C and 60% RH

APPENDIX B: EXPERIMENTAL PROCEDURES

Blend Processing

Extrusion

For a single-screw extruder, assuming the extruder was initially purged with polyethylene:

1. Turn on the main power supply, open the cooling water tap and set the temperature. (The temperature profile will depend on the formulation of the blend.)
2. Purge the extruder using this 100% HDPE with a high MFI so as to push out the high-molecular-weight HDPE which is used for cleaning the extruder.
3. Stop the extruder and decrease the temperature settings to the intermediate values set for the respective blends to be extruded.
4. Fill the hopper with dry blend/TPS mixed with polyamide granules or with PVB shavings.
5. Turn the screw on and maintain the screw rate at 30 r/min.
6. Extrude all of the starch/polymer mix. (The extrudate is air-cooled and manually coiled after exiting extruder. This prevents the extrudate from forming lumps, resulting in long strands that can be pelletised.)
7. Monitor the current (torque) in the extruder and ensure that it does not exceed 10 amps. If it does, then proceed with emergency shut-down procedures.
8. Maintain a continuous supply of material in the feed hopper.
9. Pass 100% HDPE with a high MFI, while increasing the temperature profile. Once the temperatures are high, purge with a lower-MFI HDPE material to ensure that all the TPS/polymer blends have been cleaned out of the extruder.
10. Do not leave starch in the extruder for extended periods of time as material degrades in the extruder.
11. Turn off the main power supply.
12. Leave the system to cool and after 40 minutes, turn off the cooling water supply.



Injection Moulding Machine

Start-up

1. Turn on the main power switch at the wall and at the back right of the machine.
2. Turn on the cooling water pump and adjust to the required flow.
3. Check D button for any alarms.
4. Press the temperature button to set the temperatures. Enter the password when prompted, then set the desired temperature value.
5. Start the heating.
6. Wait for the oil to heat to the setpoint temperature of 45 °C and for all temperature zones to reach the setpoint. Allow 20 minutes for the machine to equilibrate.
7. Ensure that the nozzle is in place on the barrel end and set the temperature.
8. Empty the hopper of previous material and remove dust particles.
9. Fill the hopper with the material to be injection moulded.
10. Load the correct mould and set the mould open.
11. Initially set all speeds low (for safety reasons).
12. Set the clamping force at the desired value of 500 kN – based on the mould.
13. Press the ‘speed profiles’ key and set all the values.

Operation and Optimisation

1. The soft keys from both the injection unit page and the mould set-up page can access the injection profile, the holding profile and the dosing profile pages. These pages and the process optimisation page can be used to optimise the automatic process during operation. Initially, set one value for dosing speed, injection speed and holding pressure.
2. Set the machine on either manual or automatic mode and press the start button for the procedure of injection moulding.

Shut-down

1. Clear all alarms.
2. Turn off the main power switch at the wall and at the back right of machine.
3. Leave the water pump on for an hour to allow the machine to reach room temperature.



Tensile Tests

1. Turn on the main power supply to the Lloyds machine.
2. Ensure that the 5 kN load cell is connected to the machine.
3. Set the test conditions for extension to 5 mm/min.
4. Input the sample shape and dimensions and specify the number of replicates.
5. Balance the load.
6. Shut the grips until they are touching and reset the extension distance to zero.
7. Open the grips to the desired gap.
8. Reset the distance to zero.
9. Balance the load.
10. Place the sample between the grips and ensure that it is vertical.
11. Start the test.
12. Remove the sample after it has snapped and the test is complete.
13. Reset the gap between the plates.
14. Balance the load.
15. Place the next sample between the grips and start the next test.
16. When testing of all the samples is complete, save the data and exit Merlin.
17. Turn off the main power supply.



APPENDIX C: RAW DATA ON TENSILE TESTS

Table C1: TPS-PVB blends – day 1 data

| Mass Fraction | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------------|------|--------------|-----------|-----------------------|-----------|------------------------|-----------|
| PVB | TPS | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0 | 1 | 127.41 | 5.85 | 6.47 | 2.02 | 31.50 | 7.06 |
| 0.08 | 0.92 | 139.12 | 2.12 | 6.90 | 0.67 | 32.55 | 1.58 |
| 0.22 | 0.78 | 91.87 | 5.84 | 4.61 | 3.49 | 31.34 | 7.37 |
| 0.50 | 0.5 | 30.82 | 6.28 | 3.06 | 5.69 | 228.72 | 11.11 |
| 0.78 | 0.22 | 8.69 | 7.46 | 13.90 | 5.85 | 364.39 | 4.08 |
| 0.92 | 0.08 | 5.52 | 11.48 | 9.12 | 13.07 | 345.68 | 3.24 |
| 1 | 0 | 2.98 | 0.15 | 7.54 | 0.55 | 346.03 | 14.69 |

Table C2: TPS-PVB blends – day 3 data

| Mass Fraction | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------------|------|--------------|-----------|-----------------------|-----------|------------------------|-----------|
| PVB | TPS | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0 | 1 | 193.37 | 3.37 | 8.46 | 3.25 | 24.93 | 1.49 |
| 0.08 | 0.92 | 189.71 | 2.54 | 8.61 | 1.39 | 27.30 | 2.60 |
| 0.22 | 0.78 | 124.22 | 4.20 | 5.44 | 5.03 | 26.91 | 5.78 |
| 0.50 | 0.5 | 39.19 | 17.17 | 4.01 | 7.57 | 195.12 | 31.10 |
| 0.78 | 0.22 | 7.46 | 17.37 | 13.61 | 18.06 | 369.20 | 2.93 |
| 0.92 | 0.08 | 5.30 | 12.62 | 9.47 | 10.32 | 353.57 | 3.37 |
| 1 | 0 | 4.77 | 8.58 | 8.81 | 7.69 | 389.78 | 3.91 |



Table C3: TPS-PVB blends – day 7 data

| Mass Fraction | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------------|------|--------------|-----------|-----------------------|-----------|------------------------|-----------|
| PVB | TPS | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0 | 1 | 283.16 | 3.30 | 10.69 | 3.09 | 20.05 | 4.06 |
| 0.08 | 0.92 | 243.79 | 2.25 | 9.74 | 1.62 | 23.05 | 5.34 |
| 0.22 | 0.78 | 161.27 | 4.54 | 6.30 | 3.13 | 22.63 | 8.04 |
| 0.50 | 0.5 | 41.70 | 4.87 | 4.39 | 3.45 | 267.51 | 5.02 |
| 0.78 | 0.22 | 8.83 | 2.61 | 14.36 | 3.30 | 345.26 | 1.24 |
| 0.92 | 0.08 | 4.89 | 9.82 | 8.39 | 11.56 | 318.23 | 5.46 |
| 1 | 0 | 4.06 | 8.12 | 6.91 | 5.60 | 328.38 | 2.03 |

Table C4: TPS-PVB blends – day 14 data

| Mass Fraction | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------------|------|--------------|-----------|-----------------------|-----------|------------------------|-----------|
| PVB | TPS | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0 | 1 | 269.68 | 8.00 | 10.03 | 7.35 | 15.54 | 27.77 |
| 0.08 | 0.92 | 227.18 | 9.04 | 9.79 | 3.73 | 19.18 | 9.59 |
| 0.22 | 0.78 | 143.43 | 1.78 | 6.56 | 3.39 | 24.14 | 10.18 |
| 0.50 | 0.5 | 40.51 | 11.42 | 4.62 | 3.19 | 216.90 | 14.07 |
| 0.78 | 0.22 | 6.82 | 2.25 | 12.86 | 2.59 | 380.18 | 2.81 |
| 0.92 | 0.08 | 4.05 | 8.88 | 7.34 | 7.51 | 359.67 | 4.02 |
| 1 | 0 | 3.99 | 10.07 | 7.26 | 10.07 | 374.93 | 4.83 |



Table C5: TPS-PVB blends – day 21 data

| Mass Fraction | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------------|------|--------------|-----------|-----------------------|-----------|------------------------|-----------|
| PVB | TPS | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0 | 1 | 267.27 | 3.63 | 10.49 | 1.40 | 16.79 | 0.76 |
| 0.08 | 0.92 | 145.53 | 0 | 8.89 | 0 | 22.47 | 0 |
| 0.22 | 0.78 | 145.01 | 12.35 | 5.89 | 4.37 | 23.46 | 8.02 |
| 0.50 | 0.5 | 45.34 | 5.23 | 3.49 | 2.57 | 241.05 | 16.07 |
| 0.78 | 0.22 | 5.86 | 5.39 | 10.38 | 7.63 | 409.13 | 2.67 |
| 0.92 | 0.08 | 2.46 | 15.91 | 5.49 | 12.83 | 396.46 | 4.43 |
| 1 | 0 | 1.61 | 4.46 | 2.97 | 12.37 | 332.93 | 7.27 |

Table C6: TPS-PVB blends – day 30 data

| Mass Fraction | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------------|------|--------------|-----------|-----------------------|-----------|------------------------|-----------|
| PVB | TPS | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0 | 1 | 314.99 | 0 | 10.35 | 0 | 13.31 | 0 |
| 0.22 | 0.78 | 149.09 | 6.77 | 6.22 | 3.73 | 19.71 | 5.38 |
| 0.50 | 0.5 | 44.38 | 3.46 | 3.47 | 4.04 | 255.95 | 7.35 |
| 0.78 | 0.22 | 5.42 | 7.66 | 9.95 | 7.12 | 409.30 | 2.37 |
| 0.92 | 0.08 | 1.84 | 15.72 | 3.65 | 14.85 | 353.29 | 3.67 |
| 1 | 0 | 1.56 | 12.49 | 1.37 | 10.36 | 205.94 | 19.84 |



PVB-Euremelt blends

Table C7: PVB-E2138 blends – day 1 data

| Mass Fraction | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------------|------|--------------|-----------|-----------------------|-----------|------------------------|-----------|
| E2138 | PVB | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0.0 | 1 | 3.2 | 15.41 | 6.10 | 11.15 | 335 | 4 |
| 0.25 | 0.75 | 2.7 | 12.20 | 3.86 | 15.90 | 364 | 7 |
| 0.5 | 0.5 | 6.8 | 9.24 | 5.30 | 2.72 | 417 | 1 |
| 0.75 | 0.25 | 21.1 | 3.30 | 2.97 | 2.94 | 260 | 7 |
| 1.0 | 0 | 30.9 | 4.9 | 4.0 | 2.3 | 459.7 | 6.1 |

Table C8: PVB-E2138 blends – day 17 data

| Mass Fraction | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------------|------|--------------|-----------|-----------------------|-----------|------------------------|-----------|
| E2138 | PVB | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0.0 | 1 | 4.05 | 8.88 | 7.34 | 7.51 | 359.67 | 4.02 |
| 0.3 | 0.75 | 3.80 | 8.10 | 3.11 | 5.14 | 320.82 | 2.55 |
| 0.5 | 0.5 | 7.80 | 12.97 | 3.98 | 2.50 | 370.47 | 2.83 |
| 0.8 | 0.25 | 25.31 | 6.41 | 2.96 | 3.69 | 238.48 | 2.51 |
| 1.0 | 0 | 32.59 | 12.08 | 3.76 | 2.39 | 356.82 | 18.90 |



Table C9: PVB-E2138 blends – day 51 data

| Mass Fraction | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------------|------|--------------|-----------|-----------------------|-----------|------------------------|-----------|
| E2138 | PVB | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0.25 | 0.75 | 3.0 | 1 | 3 | 0 | 344 | 6 |
| 0.50 | 0.5 | 7.1 | 0 | 4 | 0 | 367 | 22 |
| 0.75 | 0.25 | 24.9 | 0 | 3 | 1 | 235 | 16 |
| 1 | 0 | 31.2 | 1 | 4 | 0 | 292 | 26 |

Table C10: PVB-E2140 blends – day 1 data

| Mass Fraction | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------------|------|--------------|---------------|-----------------------|---------------|------------------------|---------------|
| E2140 | PVB | Average | Std.Dev, % | Average | Std.Dev, % | Average | Std.Dev, % |
| 0 | 1 | 3.23 | 15.41 | 6.10 | 11.15 | 335.23 | 4.18 |
| 0.25 | 0.75 | 2.05 | 12.37 | 2.17 | 6.88 | 405.04 | 9.44 |
| 0.5 | 0.5 | 3.41 | 5.67 | 2.55 | 3.14 | 382.36 | 7.39 |
| 0.75 | 0.25 | 8.43 | 8.72 | 2.78 | 1.40 | 314.18 | 4.61 |
| 1 | 0 | 15.35 | 0.06 | 5.25 | 10.30 | 509.72 | 3.07 |

Table C11: PVB-E2140 blends – day 14 data

| Mass Fraction | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------------|------|--------------|-----------|-----------------------|-----------|------------------------|-----------|
| E2140 | PVB | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0 | 1 | 4 | 8.88 | 7.3 | 7.5 | 359.7 | 4.0 |
| 0.25 | 0.75 | 4 | 10.10 | 2 | 8 | 323 | 9 |
| 0.5 | 0.5 | 2 | 3.87 | 2 | 10 | 388 | 6 |
| 0.75 | 0.25 | 9 | 4.45 | 2 | 4 | 272 | 12 |
| 1 | 0 | 17 | 0.00 | 4 | 0 | 499 | 0 |



Table C12: PVB-E2140 blends – day 30 data

| Mass Fraction | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------------|------|--------------|-----------|-----------------------|-----------|------------------------|-----------|
| E2140 | PVB | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0 | 1 | 2 | 12.5 | 1.4 | 10.4 | 205.9 | 19.8 |
| 0.25 | 0.75 | 4 | 7.1 | 3 | 3.1 | 385 | 5 |
| 0.5 | 0.5 | 5 | 8.0 | 3 | 3.5 | 345 | 4 |
| 0.75 | 0.25 | 11 | 10.0 | 3 | 1.6 | 295 | 3 |
| 1 | 0 | 17 | 3.0 | 5 | 0.1 | 486 | 2 |

Table C13: TPS-E2140 blends – day 1 data

| Mass Fraction | | Young's Modulus (MPa) | | Tensile Strength (MPa) | | Elongation-to-break, % | |
|---------------|------|-----------------------|-----------|------------------------|-----------|------------------------|-----------|
| E2140 | TPS | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0 | 1 | 127.4 | 6 | 6 | 2 | 31 | 7 |
| 0.08 | 0.92 | 95.3 | 9 | 6 | 7 | 45 | 14 |
| 0.22 | 0.78 | 39.0 | 11 | 3 | 4 | 112 | 4 |
| 0.50 | 0.5 | 25.2 | 4 | 2 | 7 | 169 | 14 |
| 0.78 | 0.22 | 21.5 | 14 | 2 | 8 | 371 | 20 |
| 0.92 | 0.08 | 18.4 | 7 | 2 | 3 | 479 | 13 |
| 1 | 0 | 3.2 | 15 | 6 | 11 | 335 | 4 |



Table C14: TPS-E2140 blends – day 14 data

| Mass Fraction | | Young's Modulus (MPa) | | Tensile Strength (MPa) | | Elongation-to-break, % | |
|---------------|------|-----------------------|-----------|------------------------|-----------|------------------------|-----------|
| E2140 | TPS | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0 | 1 | 269.7 | 8 | 10 | 7 | 16 | 27.8 |
| 0.08 | 0.92 | 181.4 | 10 | 9 | 6 | 31 | 27.7 |
| 0.22 | 0.78 | 75.1 | 7 | 5 | 3 | 82 | 17.0 |
| 0.50 | 0.5 | 35.9 | 8 | 2 | 15 | 107 | 9.4 |
| 0.78 | 0.22 | 24.9 | 10 | 2 | 7 | 389 | 20.4 |
| 0.92 | 0.08 | 20.4 | 6 | 2 | 7 | 319 | 7.1 |
| 1 | 0 | 4.0 | 10 | 7 | 10 | 375 | 4.8 |

Table C15: TPS-E2140 blends – day 30 data

| Mass Fraction | | Young's Modulus (MPa) | | Tensile Strength (MPa) | | Elongation-to-break, % | |
|---------------|------|-----------------------|-----------|------------------------|-----------|------------------------|-----------|
| E2140 | TPS | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0 | 1 | 315.0 | 0 | 10 | 0 | 13 | 0 |
| 0.08 | 0.92 | 133.1 | 6 | 7 | 6 | 31 | 8 |
| 0.22 | 0.78 | 64.3 | 12 | 5 | 5 | 76 | 12 |
| 0.50 | 0.5 | 20.9 | 10 | 2 | 9 | 322 | 27 |
| 0.78 | 0.22 | 17.0 | 8 | 2 | 15 | 271 | 30 |
| 0.92 | 0.08 | 3.2 | 15 | 6 | 11 | 335 | 4 |
| 1 | 0 | 315.0 | 0 | 10 | 0 | 13 | 0 |



Table C16: TPS - E2138 blends – day 1 data

| Mass Fraction | | Young's Modulus (MPa) | | Tensile Strength (MPa) | | Elongation-to-break, % | |
|---------------|------|-----------------------|------------|------------------------|------------|------------------------|------------|
| E 2138 | TPS | Average | Std. Dev,% | Average | Std. Dev,% | Average | Std. Dev,% |
| 0 | 1 | 127.4 | 5.85 | 6.47 | 2.02 | 31 | 7 |
| 0.8 | 0.92 | 84.6 | 8.27 | 4.45 | 0.08 | 23 | 2 |
| 0.22 | 0.78 | 62.2 | 7.57 | 4.48 | 0.52 | 46 | 5 |
| 0.5 | 0.5 | 48.5 | 4.70 | 2.60 | 0.42 | 61 | 11 |
| 0.78 | 0.22 | 26.0 | 2.13 | 1.80 | 0.14 | 109 | 17 |
| 1 | 0 | 18.9 | 0.00 | 2.97 | 0.00 | 205 | 0 |

Table C17: TPS - E2138 blends – day 7 data

| Mass Fraction | | Young's Modulus (MPa) | | Tensile Strength (MPa) | | Elongation-to-break, % | |
|---------------|------|-----------------------|-----------|------------------------|-----------|------------------------|-----------|
| E 2138 | TPS | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0 | 1 | 283.16 | 3.30 | 10.69 | 3.09 | 20.05 | 4.06 |
| 0.8 | 0.92 | 171.18 | 2.13 | 7.90 | 17.27 | 17.39 | 4.55 |
| 0.22 | 0.78 | 117.88 | 7.02 | 5.51 | 5.00 | 29.97 | 17.42 |
| 0.5 | 0.5 | 48.90 | 12.65 | 2.32 | 15.16 | 59.05 | 15.74 |
| 0.78 | 0.22 | 32.80 | 11.16 | 2.47 | 11.05 | 99.90 | 10.94 |
| 1 | 0 | 3.23 | 15.41 | 6.10 | 11.15 | 335.23 | 4.18 |



Table C18: TPS - E2138 blends – day 35 data

| Mass Fraction | | Young's Modulus (MPa) | | Tensile Strength (MPa) | | Elongation-to-break, % | |
|---------------|------|-----------------------|-----------|------------------------|-----------|------------------------|-----------|
| E2138 | TPS | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0.8 | 0.92 | 179.3 | 14 | 6.78 | 0 | 11 | 1 |
| 0.22 | 0.78 | 123.3 | 13 | 6.54 | 3 | 23 | 10 |
| 0.5 | 0.5 | 49.3 | 2 | 3.23 | 0 | 40 | 5 |
| 0.78 | 0.22 | 35.0 | 1 | 2.29 | 0 | 77 | 0 |
| 1 | 0 | 3.2 | 15 | 6.10 | 0 | 335 | 4 |

Table C19: TPS-PVB-E2140 blends – day 1 data

| Mass Fraction | | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------------|------|--------|--------------|-----------|-----------------------|-----------|------------------------|-----------|
| TPS | PVB | Eu2140 | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 1 | 0 | 0 | 127 | 5.9 | 6.5 | 2.0 | 31.5 | 7.1 |
| 0.67 | 0.17 | 0.17 | 26 | 1.9 | 2.1 | 0.1 | 207.5 | 6.1 |
| 0.33 | 0.33 | 0.33 | 5 | 0.2 | 1.4 | 0.0 | 353.9 | 30.5 |
| 0.16 | 0.17 | 0.67 | 12 | 0.8 | 1.2 | 0.0 | 242.3 | 29.4 |
| 0.17 | 0.67 | 0.17 | 2 | 0.2 | 1.5 | 0.2 | 450.7 | 24.5 |



Table C20: TPS-PVB-E2140 blends – day 14 data

| Mass Fraction | | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------------|------|-------|--------------|-----------|-----------------------|-----------|------------------------|-----------|
| TPS | PVB | E2140 | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 1 | 0 | 0 | 269.68 | 8.00 | 10.03 | 7.35 | 15.54 | 27.77 |
| 0.66 | 0.17 | 0.17 | 47 | 4.4 | 4.2 | 0.2 | 176.7 | 8.9 |
| 0.33 | 0.33 | 0.33 | 7 | 0.4 | 2.3 | 0.1 | 349.4 | 12.0 |
| 0.17 | 0.17 | 0.67 | 12 | 2.4 | 2.2 | 0.1 | 388.8 | 79.5 |
| 0.17 | 0.67 | 0.17 | 2 | 0.2 | 3.1 | 0.3 | 404.3 | 23.3 |

Table C21: TPS-PVB-E2140 blends – day 30 data

| Mass, % | | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------|------|-------|--------------|-----------|-----------------------|-----------|------------------------|-----------|
| TPS | PVB | E2140 | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 100 | 0 | 0 | 315 | 0 | 10.4 | 0 | 13.3 | 0 |
| 66.8 | 16.6 | 16.6 | 49 | 2.6 | 4.2 | 0.1 | 150.4 | 3.4 |
| 33.3 | 33.3 | 33.3 | 9 | 0.9 | 2.3 | 0.1 | 356.9 | 14.4 |
| 16.6 | 16.6 | 66.8 | 14 | 0.8 | 1.5 | 0.2 | 212.7 | 22.1 |
| 16.5 | 66.8 | 16.6 | 3 | 0.2 | 3.1 | 0.2 | 431.1 | 18.2 |



Table C22: TPS-PVB-anhydride blends – day 1 data

| Mass, % | | Mass Fraction | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------|------|---------------|---------|--------------|---------|-----------------------|---------|------------------------|--|
| TPS | PVB | Anhydride | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% | |
| 0 | 0 | 0 | 127 | 5.9 | 6.5 | 2.0 | 31.5 | 7.1 | |
| 0.92 | 0 | 0.08 | 135 | 3.0 | 7.9 | 1.5 | 29.3 | 6.8 | |
| 0.78 | 0.11 | 0.11 | 79 | 18.8 | 3.9 | 7.4 | 17.2 | 14.3 | |
| 0.5 | 0.25 | 0.25 | 57 | 16.6 | 3.4 | 2.6 | 33.2 | 5.0 | |
| 0.39 | 0.38 | 0.25 | 36 | 19.5 | 3.8 | 1.9 | 111.4 | 1.4 | |
| 0.25 | 0.5 | 0.25 | 8 | 16.3 | 6.5 | 5.7 | 219.1 | 1.5 | |
| 0.11 | 0.64 | 0.25 | 6 | 3.5 | 10.0 | 2.2 | 265.1 | 1.8 | |

Table C23: TPS-PVB-anhydride blends – day 3 data

| Mass, % | | Mass Fraction | | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------|-----|---------------|---------|--------------|---------|-----------------------|---------|------------------------|--|
| TPS | PVB | Anhydride | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% | |
| 100 | 0 | 0 | 193.4 | 3.0 | 8.0 | 3.0 | 25.0 | 1.0 | |
| 92 | 0 | 8 | 205 | 4.8 | 9.9 | 2.0 | 25.9 | 4.8 | |
| 78 | 11 | 11 | 129 | 19.2 | 4.5 | 2.7 | 12.9 | 12.1 | |
| 50 | 25 | 25 | 70 | 7.5 | 3.7 | 3.0 | 34.2 | 6.7 | |
| 39 | 38 | 25 | 35 | 18.1 | 3.4 | 2.6 | 108.0 | 9.5 | |
| 25 | 50 | 25 | 7 | 11.5 | 6.5 | 3.1 | 233.9 | 1.1 | |
| 11 | 64 | 25 | 5 | 5.1 | 8.9 | 2.2 | 283.9 | 2.1 | |



Table C24: TPS-PVB-anhydride blends – day 7 data

| Mass, % | | Mass Fraction | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------|-----------|---------------|--------------|-----------|-----------------------|-----------|------------------------|-----------|
| PVB | Anhydride | TPS | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0 | 0 | 1 | 283.2 | 3.3 | 10.7 | 3.1 | 20.0 | 4.1 |
| 0 | 8 | 0.92 | 286 | 12.0 | 12.0 | 0.0 | 20.2 | 2.0 |
| 11 | 11 | 0.78 | 157 | 2.8 | 5.8 | 0.2 | 14.1 | 2.0 |
| 25 | 25 | 0.5 | 85 | 4.0 | 4.4 | 0.1 | 32.3 | 1.4 |
| 38 | 25 | 0.39 | 44 | 285.8 | 4.3 | 0.1 | 106.3 | 20.2 |
| 50 | 25 | 0.25 | 7 | 0.6 | 7.5 | 0.5 | 222.2 | 5.3 |
| 64 | 25 | 0.11 | 7 | 0.1 | 11.0 | 0.2 | 263.3 | 5.2 |

Table C25: TPS-PVB-anhydride blends – day 14 data

| Mass, % | | Mass Fraction | Modulus, MPa | | Tensile Strength, MPa | | Elongation-to-break, % | |
|---------|----------|---------------|--------------|-----------|-----------------------|-----------|------------------------|-----------|
| % PVB | % gypsum | TPS | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0 | 0 | 1 | 269.68 | 8.00 | 10.03 | 7.35 | 15.54 | 27.77 |
| 0 | 8 | 0.92 | 268.42 | 7.25 | 12.47 | 0.15 | 22.23 | 0.55 |
| 11 | 11 | 0.78 | 248.34 | 78.18 | 5.12 | 0.31 | 12.77 | 1.94 |
| 25 | 25 | 0.5 | 99.29 | 13.58 | 4.41 | 0.01 | 29.57 | 2.32 |
| 38 | 25 | 0.39 | 42.29 | 7.87 | 4.01 | 0.13 | 123.07 | 13.10 |
| 50 | 25 | 0.25 | 10.70 | 4.48 | 7.03 | 1.11 | 293.84 | 55.70 |
| 64 | 25 | 0.11 | 6.27 | 0.38 | 10.61 | 0.38 | 285.27 | 3.64 |



Table C26: TPS-E2140-Anhydride blends – day 30 data

| Mass, % | | Mass Fraction | Modulus, MPa | | Tensile Strength, Ma | | Elongation-to-break, % | |
|---------|-----------|---------------|--------------|-----------|----------------------|-----------|------------------------|-----------|
| PVB | Anhydride | TPS | Average | Std.Dev,% | Average | Std.Dev,% | Average | Std.Dev,% |
| 0 | 0 | 1 | 314.99 | 0 | 10.35 | 0 | 13.31 | 0 |
| 0 | 8 | 0.92 | 255.95 | 23.41 | 10.90 | 0.18 | 21.74 | 0.47 |
| 11 | 11 | 0.78 | 154.25 | 20.10 | 5.15 | 0.75 | 14.39 | 5.76 |
| 25 | 25 | 0.5 | 135.69 | 17.26 | 4.13 | 0.12 | 21.25 | 1.54 |
| 38 | 25 | 0.39 | 34.48 | 8.26 | 3.44 | 0.23 | 88.81 | 21.24 |
| 50 | 25 | 0.25 | 5.64 | 0.41 | 4.99 | 0.41 | 259.99 | 13.24 |
| 64 | 25 | 0.11 | 4.59 | 0.26 | 8.50 | 0.58 | 287.83 | 22.68 |