



UNIVERSITEIT VAN PRETORIA  
UNIVERSITY OF PRETORIA  
YUNIBESITHI YA PRETORIA

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

**By**

**CORDELIA CHADEHUMBE**

**A thesis**

**Submitted in partial fulfilment of the requirements**

**for the degree**

**Philosophiae Doctor in Chemical Engineering**

**UNIVERSITY OF PRETORIA**

Supervisor:

Professor W. W. Focke

August 2006



## ABSTRACT

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

by

Cordellia Chadehumbe

Supervisor:

Prof. W. W. Focke

Department of Chemical Engineering

for the degree Philosophiae Doctor

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 HiMaize<sup>TM</sup>, 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



## ACKNOWLEDGEMENTS

Firstly, I would like to thank my supervisor, Professor Walter Focke, for his experience and guidance throughout the duration of my studies. I greatly appreciate his continuous enthusiasm and willingness to assist, especially when I started working and had very little time to work on my dissertation.

Sincere thanks to my children, Vladi and Videlle Sita, for spending time on their own playing while Mommy had to do her work. This dissertation is dedicated to my parents, Walton and Beatrice Chadehumbe, who played a major role in my education from the beginning and who encouraged me to pursue a PhD when I thought I had had enough of studying.

Acknowledgments also go to Mara Burns who helped me with some of my experiments when I started working; to the Centre for Microscopy and Microanalysis for their kindness and assistance with the scanning electron microscopy; and to Dr Sabina Verryn for assistance with the X-ray diffraction analysis.

Financial support for this research from the Third World Organisation for Women in Science, the THRIP programme of the Department of Trade and Industry, the National Research Foundation of South Africa, and from African Products (Pty) Ltd is gratefully acknowledged and appreciated. Finally but not least I would like to thank God the Almighty for his word tells us in Zachariah 4:6 "Not by power nor by might but my spirit, says the Lord."



## TABLE OF CONTENTS

<b>ABSTRACT .....</b>	<b>I</b>
<b>ACKNOWLEDGEMENTS.....</b>	<b>III</b>
<b>LIST OF FIGURES .....</b>	<b>VI</b>
<b>LIST OF TABLES .....</b>	<b>IX</b>
<b>DEFINITIONS .....</b>	<b>XI</b>
<b>LIST OF ABBREVIATIONS.....</b>	<b>XIII</b>
<b>1 INTRODUCTION.....</b>	<b>14</b>
1.1 SCOPE OF THE WORK .....	16
<b>2 LITERATURE REVIEW.....</b>	<b>17</b>
2.1 BIOPOLYMERS .....	17
2.2 STARCH STRUCTURE AND PROPERTIES.....	17
2.3 STARCH GELATINISATION.....	19
2.4 STARCH MODIFICATION.....	20
2.4.1 <i>Modifications aimed at changing the amylose/amylopectin content .....</i>	<i>20</i>
2.4.2 <i>Modification by controlled degradation .....</i>	<i>20</i>
2.4.3 <i>Pregelatinisation.....</i>	<i>21</i>
2.4.4 <i>Cross-linking.....</i>	<i>21</i>
2.4.5 <i>Cationisation.....</i>	<i>21</i>
2.4.6 <i>Acetylating.....</i>	<i>22</i>
2.4.7 <i>Dextrinisation.....</i>	<i>22</i>
2.4.8 <i>Grafting.....</i>	<i>22</i>
2.5 STARCH AS A THERMOPLASTIC MATERIAL.....	23
2.5.1 <i>Effect of relative humidity.....</i>	<i>24</i>
2.5.2 <i>Effect of plasticisers.....</i>	<i>25</i>
2.5.3 <i>Effect of ageing.....</i>	<i>29</i>
2.6 STARCH-FILLED PLASTICS .....	29
2.7 STARCH BLENDS.....	30
2.8 STARCH-BASED NANO-COMPOSITES .....	31
<b>3 EXPERIMENTAL .....</b>	<b>33</b>
3.1 EXPERIMENTAL DESIGN.....	33
3.2 MATERIALS .....	34
3.3 SAMPLE PREPARATION.....	36



3.4	CHARACTERISATION .....	41
3.4.1	<i>Tensile tests</i> .....	41
3.4.2	<i>Dynamic mechanical analysis (DMA)</i> .....	42
3.4.3	<i>X-ray diffraction (XRD)</i> .....	43
3.4.4	<i>Scanning electron microscopy (SEM)</i> .....	43
3.4.5	<i>Water resistance</i> .....	44
3.4.6	<i>Melt flow index</i> .....	44
<b>4</b>	<b>RESULTS AND DISCUSSION</b> .....	<b>45</b>
4.1	THERMOPLASTIC STARCH .....	45
4.1.1	<i>Extrusion</i> .....	45
4.1.2	<i>Evaluation of plasticisers</i> .....	46
4.1.3	<i>Effect of starch source on the mechanical properties</i> .....	48
4.1.4	<i>Effect of filler</i> .....	52
4.2	TPS-PVB BLENDS.....	53
4.3	PVB-POLYAMIDE BLENDS .....	61
4.4	TPS-POLYAMIDE BLENDS .....	63
4.5	TPS-PVB-POLYAMIDE SYSTEMS .....	71
4.6	TPS-PVB-ANHYDRIDE SYSTEMS .....	74
<b>5</b>	<b>CONCLUSIONS</b> .....	<b>77</b>
	<b>REFERENCES</b> .....	<b>79</b>
	<b>APPENDICES</b> .....	<b>83</b>
	<b>APPENDIX A: X-RAY DIFFRACTION SPECTRA</b> .....	<b>84</b>
	<b>APPENDIX B: EXPERIMENTAL PROCEDURES</b> .....	<b>90</b>
	<b>APPENDIX C: RAW DATA ON TENSILE TESTS</b> .....	<b>93</b>



## LIST OF FIGURES

Figure 1:	Structure of amylose [African Products, s.a.] .....	18
Figure 2:	Structure of amylopectin [African Products, s.a].....	18
Figure 3:	Illustration of the gelatinisation process [African Products, s.a.] .....	20
Figure 4:	Water uptake as a function of glycerol content and equilibrium relative humidity [Van Soest & Knooren, 1997] .....	25
Figure 5:	Effect of glycerol on the processing window of cornstarch [Liu <i>et al.</i> , 2001].....	26
Figure 6:	Schematic illustration of the effect of glycerol content on the tensile strength of potato starch [Yu <i>et al.</i> , 1998] .....	27
Figure 7:	Schematic diagram illustrating the effect of glycerol content on elongation-to-break [Yu <i>et al.</i> , 1998] .....	28
Figure 8:	Preparation of a starch-based nano-composite.....	31
Figure 9:	Experimental design.....	33
Figure 10:	Papenmeier high-speed mixer .....	37
Figure 11:	Rapra single-screw extruder .....	38
Figure 12:	Engel 3040 screw-type injection moulder .....	40
Figure 13:	Typical tensile stress-strain curves for plastics .....	41
Figure 14:	Effect of ageing at 30°C and 60% RH on the elongation-at-break .....	48
Figure 15:	Effect of ageing at 30°C and 60% RH on TPS tensile strength .....	50
Figure 16:	Effect of glycerol content on the breaking strain of normal maize-based TPS aged at 23 °C and 44% RH.....	51
Figure 17:	Effect of glycerol content on the tensile strength of normal maize-based TPS aged at 23 °C and 44% RH.....	51
Figure 18:	Effect of ageing at 30 °C and 60% RH on the mechanical properties of TPS- PVB blends .....	55
Figure 19:	Effect of water soak on the tensile strength of TPS-PVB blends.....	56
Figure 20:	Tan $\delta$ (loss factor) at 10 Hz for TPS-PVB blends aged at 30 °C and 60% RH for at least 30 days .....	56
Figure 21:	XRD spectra of TPS-PVB blends aged for 30 days at 30 °C and 60% RH .....	57
Figure 22:	Scanning electron micrograph of a fracture surface of the blend containing 22% TPS .....	59



Figure 23:	Scanning electron micrograph of an enzyme-eroded fracture surface of the blend containing 22% TPS .....	59
Figure 24:	Effect of ageing at 30 °C and 60% RH on the mechanical properties of PVB-Euremelt blends .....	61
Figure 25:	Effect of composition on the melt flow index (MFI) of a PVB-Euremelt blend.. ..	62
Figure 26:	Effect of ageing at 30 °C and 60% RH on the mechanical properties of TPS-polyamide blends .....	65
Figure 27:	Scanning electron micrograph of a fracture surface of the blend containing 92% E2138 .....	66
Figure 28:	Scanning electron micrograph of a fracture surface of the blend containing 92% E2140 .....	67
Figure29:	Optical micrograph of a fracture surface of the blend containing 92% E2138....	68
Figure 30:	Optical micrograph of a fracture surface of the blend containing 92% E2140	68
Figure 31:	Effect of water soak on the tensile strength of TPS-E2140 blends .....	69
Figure 32:	XRD spectra of TPS-E2140 blends aged for 30 days at 30 °C and 60% RH...	70
Figure 33:	Effect of ageing at 30 °C and 60% RH on the mechanical properties of TPS-EMS polyamide blends.....	71
Figure 34:	Effect of ageing at 30 °C and 60% RH on the tensile stress of TPS-PVB–polyamide (E2140) .....	73
Figure 35:	Effect of ageing at 30 °C and 60% RH on the elongation-to-break of TPS-PVB–polyamide (E2140) .....	73
Figure 36:	Effect of ageing at 30 °C and 60% RH on the modulus of TPS-PVB–polyamide (E2140) .....	74
Figure 37:	Effect of ageing at 30 °C and 60% RH on the mechanical properties of TPS-PVB–anhydride blends .....	76
Figure A1:	XRD spectra of the TPS-PVB blend containing 0% PVB blends at 30 °C and 60% RH .....	84
Figure A2:	XRD spectra of the TPS-PVB blend containing 22% PVB blends at 30 °C and 60% RH .....	85
Figure A3:	XRD spectra of the TPS-PVB blend containing 50% PVB blends at 30 °C and 60% RH .....	86
Figure A4:	XRD spectra of the TPS-PVB blend containing 75% PVB blends at 30 °C and 60% RH .....	87





Figure A5:	XRD spectra of the TPS-PVB blend containing 92% PVB blends at 30 °C and 60% RH .....	88
Figure A6:	XRD spectra of the TPS-PVB blend containing 100% PVB blends at 30 °C and 60% RH .....	89



## LIST OF TABLES

Table 1:	Composition of potato and maize starches .....	19
Table 2:	Amylose:amylopectin ratios of native maize and tapioca starch .....	34
Table 3:	Additives and processing aids .....	35
Table 4:	Polymers used for blending with TPS .....	35
Table 5:	Composition of the binary blends investigated .....	39
Table 6:	Composition of the TPS-PVB-E2140 ternary systems.....	40
Table 7:	Composition of the TPS-PVB-anhydride ternary systems.....	40
Table 8:	Processing window of the HiMaize™ TPS formulations using the Rapra single-screw extruder.....	46
Table 9:	Thermoplastic starch base formulation.....	48
Table 10:	Extrusion parameters TPS-PVB blends.....	53
Table 11:	Injection-moulding parameters for TPS-PVB blends.....	54
Table 12:	Extrusion parameters for TPS-E2140 blends .....	63
Table 13:	Injection moulding parameters for TPS-Euremelt [E2140 and E2138] blends	64
Table 14:	Extrusion parameters for TPS-PVB-E2140 blends .....	72
Table 15:	Injection moulding parameters for TPS-PVB-E2140 blends .....	72
Table 16:	Extrusion parameters for TPS-PVB-anhydride blends.....	75
Table 17:	Injection moulding parameters for TPS-PVB-anhydride blends.....	75
Table C1:	TPS-PVB blends – day 1 data .....	93
Table C2:	TPS-PVB blends – day 3 data .....	93
Table C3:	TPS-PVB blends – day 7 data .....	94
Table C4:	TPS-PVB blends – day 14 data .....	94
Table C5:	TPS-PVB blends – day 21 data .....	95
Table C6:	TPS-PVB blends – day 30 data .....	95
Table C7:	PVB-E2138 blends – day 1 data.....	96
Table C8:	PVB-E2138 blends – day 17 data.....	96
Table C9:	PVB-E2138 blends – day 51 data.....	97
Table C10:	PVB-E2140 blends – day 1 data.....	97
Table C11:	PVB-E2140 blends – day 14 data.....	97
Table C12:	PVB-E2140 blends – day 30 data.....	98
Table C13:	TPS-E2140 blends – day 1 data.....	98
Table C14:	TPS-E2140 blends – day 14 data.....	99



Table C15:	TPS-E2140 blends – day 30 data.....	99
Table C16:	TPS - E2138 blends – day 1 data.....	100
Table C17:	TPS - E2138 blends – day 7 data.....	100
Table C18:	TPS - E2138 blends – day 35 data.....	101
Table C19:	TPS-PVB-E2140 blends – day 1 data.....	101
Table C20:	TPS-PVB-E2140 blends – day 14 data.....	102
Table C21:	TPS-PVB-E2140 blends – day 30 data.....	102
Table C22:	TPS-PVB-anhydride blends – day 1 data.....	103
Table C23:	TPS-PVB-anhydride blends – day 3 data.....	103
Table C24:	TPS-PVB-anhydride blends – day 7 data.....	104
Table C25:	TPS-PVB-anhydride blends – day 14 data.....	104
Table C26:	TPS-E2140-Anhydride blends – day 30 data.....	105



## 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