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Mechanical properties and compostability of injection-moulded biodegradable compositions

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ABSTRACT

The aim of this project was to prepare starch-based thermoplastic compounds for biodegradable, injection-mouldable seedling tubes and golf tees. Sappi Forest Products needed partially biodegradable tubes to be able to increase the productivity of their seedlings.

The golf tee market is currently dominated by the USA, China, India and Europe and there are only a couple of South African manufacturers, who cannot cope with the market demand. Biodegradability, brittleness and low cost are what the market is looking for in the golf tees application. Brittleness is required to prevent damage to golf clubs. When the material is too hard and non-brittle, it catches under the plate of a rotary lawn mower and this causes a drag mark on the greens. Daily manual removal of the pieces is necessary, which is very labour-intensive. Preferred are highly biodegradable tees that would shatter on contact with lawn mower blades.

During the development of the seedling tubes compositions, it was found that reasonable mechanical properties in starch compounds could only be obtained with high-amylose starch. In order to further improve the material properties, blends with synthetic polymers were investigated. In this work thermoplastic starch as the main ingredient was blended with two different grades of polyamides – Euremelt 2138, EMS

Grilon BM13 SBG and also with polyvinyl butyrate (PVB) via extrusion. The addition of polymers was 20 wt% for the polyamides and 22 wt% for PVB respectively. It was found that low-molecular-weight polyamide Euremelt, the copolymer EMS Grilon and PVB form mechanically compatible blends with thermoplastic starch (TPS). The polyamides are expensive, but the recycled PVB provides a cost advantage.

Polybutylene succinate adipate (PBSA), a fully biodegradable synthetic polyester, is used as the main ingredient in golf tees applications. For cost reduction purposes urea and starch fillers were introduced into the blends. One of the blends was prepared with 40 wt% urea, the other with 20 wt% urea and 20 wt% starch. Both contained 10 wt% of stearic acid as a lubricant.

After extrusion, all compositions were injection-moulded into dumb-bell test specimens and their mechanical properties were investigated. The characterisation was further extended with X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and optical microscopy analysis. ASTM standard G160 was used to study the biodegradability of the blends through a burial test.

The specimens for tensile strength testing were aged in a humidity chamber at a relative humidity (\mathcal{RH}) of 60% at 30°C and under extreme drying conditions over phosphorous pentoxide in a desiccator at 0% \mathcal{RH} , 25°C. Starch containing blends were particularly affected by the ageing conditions, whereas polyester compositions remained stable in both environments.

The XRD and optical microscopy results point to higher crystallinity and better homogeneity of TPS and EMS Grilon than Euremelt and PVB in seedling tube compositions.

Cross-linking reactions of the starch through urea reduced the crystallinity in the golf tees. The polyester filled with urea only had higher crystallinity than the one with both starch and urea.

In seedling tubes applications, where starch is the main component, the higher crystallinity of the TPS-EMS blends brought about increased tensile strength and slower decomposition. The best decomposition was achieved in the less-crystalline TPS-PVB blend, with an 80% reduction in the elongation at break at the end of the 60-day compostability test.

When starch is introduced as filler in urea-filled polyester blends, it reduced the crystallinity of the blend and, surprisingly, also its degradability. Only 15% decomposition occurs in this composition. The polyester forms a more crystalline structure when only urea is used as filler. The higher weight loss (30%) is partly due to the leaching of urea but also indicates better compostability for this compound.

Keywords: Injection moulding, compostability, biodegradability, starch, urea, seedling tubes, golf tees.

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LIST OF ABBREVIATIONS

AAC	Aliphatic-aromatic copolyesters
ABS	Acrylonitrile-butadiene-styrene
ASTM	American Society for Testing and Materials
BDP	Biodegradable polymers
CEN	European Standardization Committee
DIN	German Institute for Standardization
DMS	Dynamic mechanical spectra
DMTA	Dynamic mechanical thermal analysis
DSC	Differential scanning calorimetry
ISO	International Standard Organization
ISR	Institute of Standards Research
NMR	Nuclear magnetic resonance
PBAT	Polybutylene adipate/terephthalate
PBS	Polybutylene succinate
PBSA	Polybutylene succinate adipate
PCL	Polycaprolactone
PET	Polyethylene terephthalate
PHA	Polyhydroxyalkanoates
PHB	Polyhydroxy butyrate
PHH	Polyhydroxyhexanoate
PHV	Polyhydroxyvalerate
PLA	Polylactic acid
PP	Polypropylene
PTMAT	Polymethylene adipate/terephthalate
PVB	Polyvinylbutyral
PVOH	Polyvinyl alcohol
\mathcal{RH}	Relative humidity
SEM	Scanning electron micrograph
Tan δ =	loss factor (loss tangent)

Tg	Glass transition temperature
TMA	Thermo-mechanical analysis
TPS	Thermoplastic starch
XRD	X-ray diffraction analysis

1 INTRODUCTION

The objective of this project was to develop injection-mouldable, low-cost biodegradable blends suitable for seedling tubes and golf tees.

Sappi Forest Products and their Research Centre at Ngodwana Nursery expressed interest in biodegradable seedling tubes. They requested such tubes to improve their productivity with the planted seedlings. As the seedlings would not have to be pulled out of the tubes before planting and less root damage would be caused, a larger number of plants would survive.

The requirements for the tube material were that they should be able to withstand 100% relative humidity (RH) for seven days at 38°C, followed by about three months spray watering, three times a week. Once planted, the tube should not restrict the growth of the plant's roots.

The current seedling tubes are made from polypropylene (PP), which can be injection-moulded with a very thin wall thickness. The material has low cost, but is non-biodegradable. Thermoplastic starch is biodegradable, but when used by itself, yields weak and moisture susceptible articles. Blends of thermoplastic starch (TPS) and polymers are considered to strengthen and increase the water resistance of the TPS material for this application.

This study is continuation of the work done by Sita (2007) who considered blends of TPS with PVB and polyamides. Starch blends are susceptible to retrogradation: the structural changes that include helix formation and crystallization that occur above the glass transition temperature. In an attempt to overcome this problem TPS was blended with polyamides and polyvinyl butyral (PVB) as modifying agents. The PVB was based on material recycled from automotive windscreens. Blending with polyamides and polyvinyl butyral improved moisture resistance, ageing behaviour, processability and mechanical properties. The mechanical properties were found to vary nonlinearly with

blend composition. This is attributed to the complex phase behaviour of the starch blends. The purpose of this study was then to evaluate practical applications of the blends systems investigated by Sita (2007).

The market for golf tees has also been growing over the past few years. With the development of the sport of golf, the demand to improve the design of golf tees is also likely to increase.

George Franklin Grant patented the golf tee in 1899 (see Figure 1). He was one of the first African-American golfers in the post-Civil War period in the USA and one of the first African-American dentists. George Grant was born in Oswego, New York, in 1847 and was the son of former slaves. He graduated from Harvard Dental School in 1870.

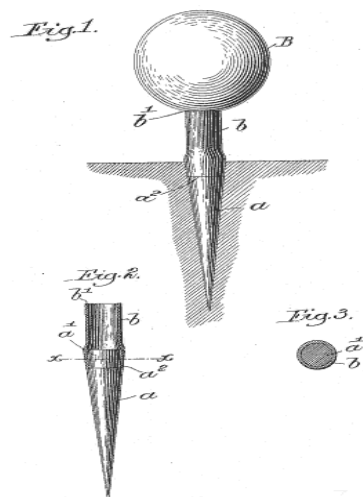


Figure 1.1: Dr Grant's golf tee

By all accounts, Dr Grant was not the most skilled golfer, but he enjoyed the recreational aspects of the game. He found the method of teeing up the ball, i.e. pinching damp sand into a launching pad, both inconsistent and tedious. This was messy and towels and water had to be provided to wash the golfer's hands. Original sand boxes can still be found on some old golf courses. George Grant was also interested in the physics of golfing and in improving the game of golf. He received US Patent No. 368,920 on 12 December 1899 for his improved golf tee.

The first commercial golf tee was the Reddy Tee invented at Maplewood Golf Club in 1921 by another American dentist, William Lovell. First manufactured in wood and painted with red tops so that they were easily seen, they were soon produced in a variety of styles and materials. The “Reddy Tee”, made of white celluloid by Nieblo Manufacturing Company, was patented in 1924. Although plastic tees are available, simple wooden tees similar to those made in the 1920s are still the most common type. History George F. Grant (s.a.6) <http://www.ourgolf.com/history/georgegrant.htm>, [2004, March 4].
Scottish Golf History (s.a.7) http://www.scottishgolfhistory.net/tee_term.htm, [2004, March 4].
Bellis, M Inventors, <http://inventors.about.com/library/inventors/blgolfteehtm.htm>, [2004, March 4].

Currently the market is dominated by the USA, China, India and Europe. South African suppliers usually import the golf tees because there are only a couple of local manufacturers, who cannot deal with the market demand.

In the interviews done with pros in golf shops around Johannesburg, we were informed that in South Africa there are about 579 golf courses. An average golf course sells 3 500 to 4 000 golf tees per month (wood and plastic). Hence, 25 to 30 million golf tees are sold every year. This is a big market, which is covered mainly by imports.

Our research led to the following South African suppliers/manufacturers: Bandit Top, Flight Simaki, Thigh less, Golf Trends and Polytron. The requirements for the golf tees are specific to the customers’ needs and may include biodegradability, brittleness, low cost, printability and colour (see Table 1.1).

Wood is biodegradable, costs the same as plastics, but could damage golf clubs, as it is hard. Polypropylene and ABS (acrylonitrile-butadiene-styrene) are non-biodegradable.

They are low cost commodity products and easily converted into products by injection moulding.

Brittleness is required to prevent golf club damage. When the material is hard and non-brittle, it catches under the plate of a rotary lawn mower and this causes a drag mark on the greens. It also blunts the lawnmower blades. Daily manual removal of the pieces is necessary, which is very labour-intensive.

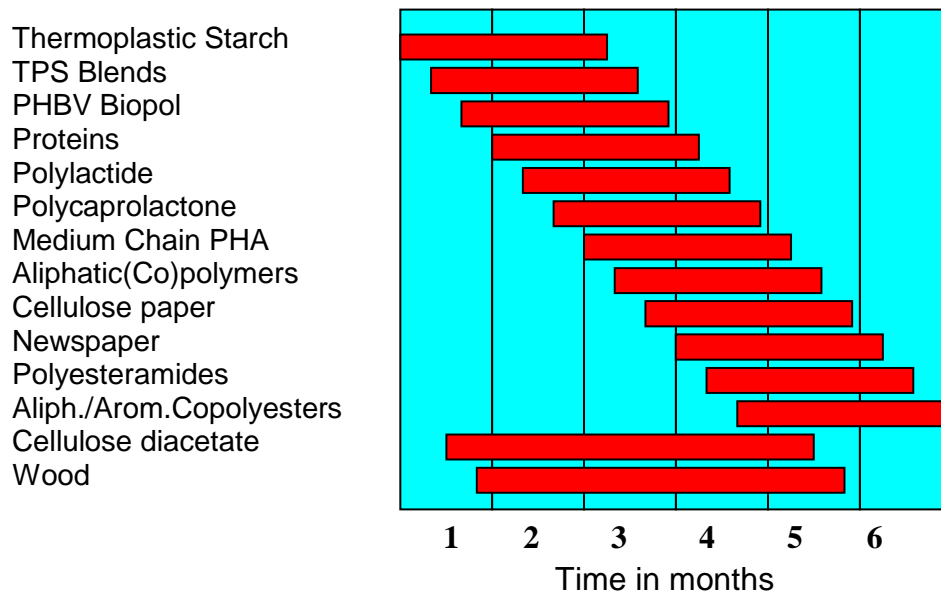


Figure 1.2: Indication of the time required for composting of various bio-based and synthetic polymeric materials

(Webber, 2000)

Table 1.1: Current golf tees and methods of production

Material	Biodegradability	Brittleness	Cost	Method of production
Wood	Biodegradable within 6 months	Brittle	Low	Wood-turning lathe
PP	Non-biodegradable	Not brittle	Low	Injection moulding
ABS	Non-biodegradable	Brittle	Low	Injection moulding

Webber (2000) published measurements of composting times for different materials performed in actively aerated and mechanically turned composting facilities (Figure 1.2). It was found that it takes one to six months for wood to degrade, while TPS, TPS blends and some biodegradable polyesters degrade within four months (Webber, 2000).

2 LITERATURE SURVEY

Polymeric materials such as conventional non-degradable polymer systems are used for high-volume applications such as packaging in the medical, automobile and agricultural areas. They can be very harmful to our environment since they do not degrade easily after their life-cycle has been completed and litter to the environment. Recycling is a better choice, but comes at a higher cost and most countries cannot afford to recycle all their polymer wastes. After recycling, the polymers' properties are poor compared with their original ones. Moreover, not all polymers can be recycled. This leads to the need for new degradable polymers, which can replace existing synthetic polymers. Replacement of these polymer systems requires that the degradable polymers have properties sufficiently comparable to those of the conventional polymers. Creating new environmentally friendly polymers or modifying existing degradable polymers can achieve these desirable properties. The term 'degradable polymers' relates to the polymeric materials that disintegrate under environmental conditions in a reasonable and demonstrable period (Narayan, Barengerg, Brash & Redpath, 1990).

Chapter1 (s.a.5) <http://scholar.lib.vt.edu/theses/available/etd-6998-172444/unrestricted/CHAPTER/1>. PDF, [2004, February 19].

2.1 MECHANISMS OF DEGRADATION

Degradation of polymers occurs by any of the following mechanisms (Swift & Glass, 1990):

Oxidative degradation: The lifetime of most polymers is determined by this mechanism. It relates to the slow oxidative degradation of polymers exposed to atmospheric oxygen. This mechanism also operates during high-temperature processing.

Biodegradation: This is promoted by enzymes and may be either aerobic or anaerobic. It provides for complete breakdown of the polymer.

Photodegradation: This requires irradiation, e.g. sunlight, and it rarely leads to complete breakdown, although small fragments may be produced for subsequent biodegradation.

Environmental erosion: This requires weather elements such as wind, rain, temperature and sunlight. It also cannot remove the polymer completely.

Chemical degradation: This requires chemical reactions using additives, e.g. metals and functional groups, which produce smaller fragments of the polymer.

However, complete removal from the environment is only possible through biodegradation

Chapter1 (s.a.5) <http://scholar.lib.vt.edu/theses/available/etd-6998-172444/unrestricted/CHAPTER/1.PDF>, [2004, February 19].

The presence of hydrolysable and/or oxidisable linkages in the polymer main chain, the presence of suitable substituents, correct stereo configuration, balance of hydrophobicity and hydrophilicity, and conformational flexibility contribute to the biodegradability of the polymers (Huang & Edelman, 1995).

Biodegradable polymers are divided into three classes:

1. Natural polymers originating from plant or animal sources (e.g. cellulose, starch, protein, collagen, etc.)
2. Certain synthetic polymers (e.g. polycaprolactone and poly-lactic acid, polyesters)
3. Biosynthetic polymers produced by fermentation processes by micro-organisms (e.g. poly-hydroxy alkanates).

Chapter1 (s.a.5) <http://scholar.lib.vt.edu/theses/available/etd-6998-172444/unrestricted/CHAPTER/1.PDF>, [2004, February 19]

Biodegradable polymers

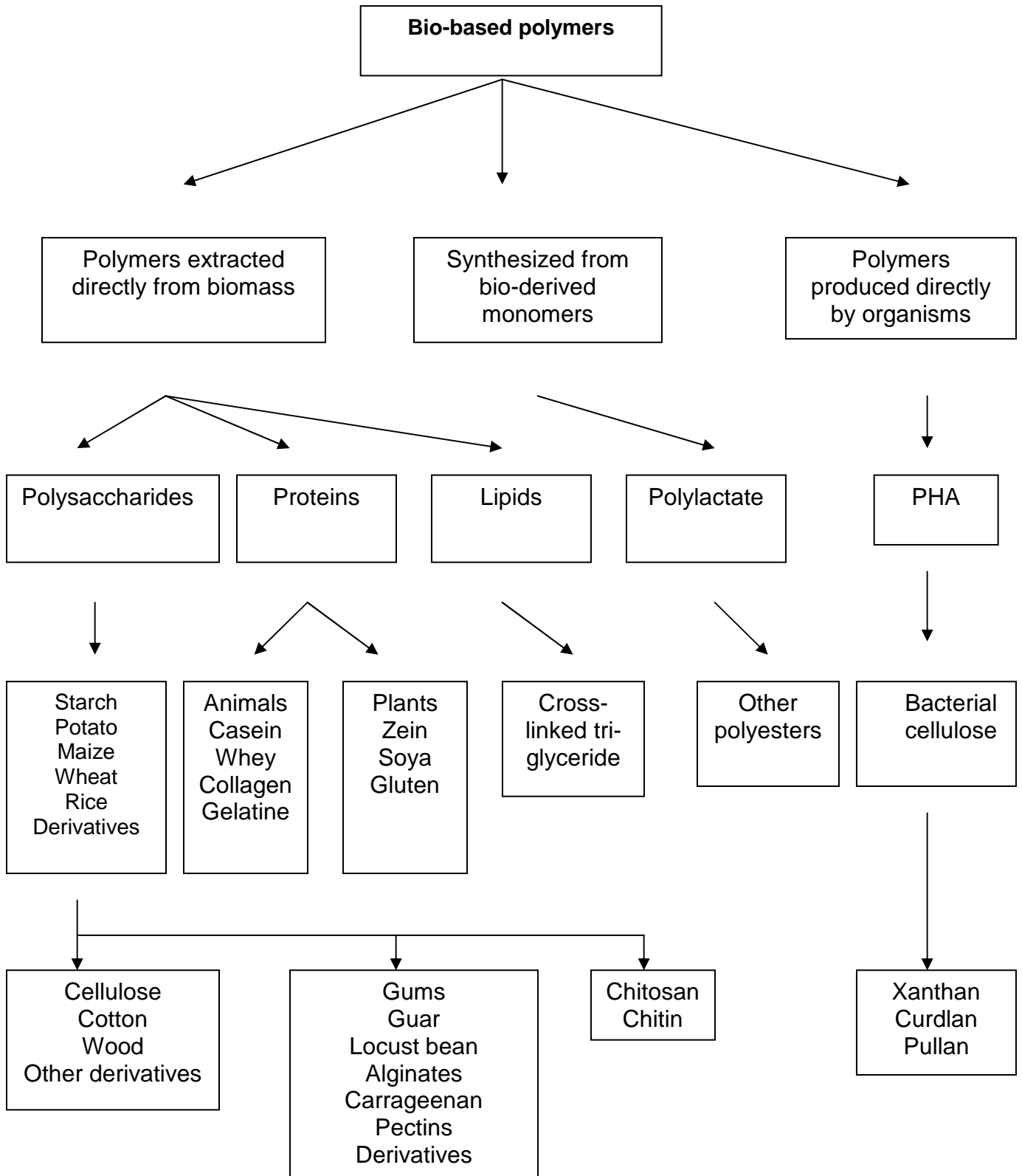


Figure 2.1: Biodegradable polymers (BDP) (Webber, 2000)

2.1.1 Starch-based compositions for seedling tubes applications

The following compositions are available for seedling tubes:

- Thermoplastic starch products(TPS)
- Starch synthetic aliphatic polyester blends
- Starch PBS/PBSA polyester blends
- Starch polyvinyl alcohol (PVOH) blends
- Starch polyvinylbutyral (PVB) blends
- Starch polyamide blends.

2.1.1.1 Starch as raw material

Starch is a natural polymer found in plants. It consists of amylose (linear polymer) (1-4 bonds) and amylopectin (branched chains) (1-4 and 1-6 bonds between the glucose repeat units) (see Figure 2.2).

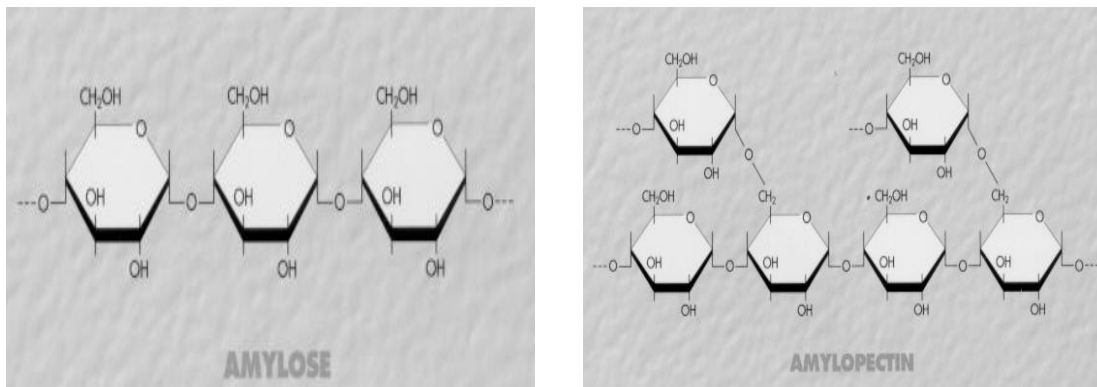


Figure 2.2: Chemical structure of amylose and amylopectin

(African Products, s.a.1)

According to the ratio of amylose to amylopectin, there are a couple of types of starch (see Table 2.1).

Table 2.1: Amylose and amylopectin content of different types of starch

Type of starch	Amylose, wt%	Amylopectin, wt%
High amylose (Hi-Maize)	70	30
Maize (Amyral/Stygel)	26	74
Cassava (tapioca)	17	83
Waxy maize	1	99

Starch is an abundant and cheap, fully biodegradable polymer, which is also an annually renewable resource and it is environmentally friendly.

The disadvantages of raw starch are that it disintegrates in water, it is not thermoplastic and cannot be melt-processed because the degradation temperature is lower than the crystalline melting point.

Starch can be modified chemically or mechanically to suit different applications. The chemical modification processes include acid modification, oxidation, cross-bonding, acetylation, cationisation and dextrinisation (African Products, s.a.2).

2.1.1.2 Thermoplastic starch

To be able to make thermoplastic material out of starch, a reduction in the hydrogen bonding between the starch molecules is needed. Raw starch can be easily converted into thermoplastic starch (TPS) or gelatinised starch with the help of a plasticiser such as water, glycerol, urea, amides, etc. Gelatinisation is a mechanical modification and can transform the crystalline form into an amorphous plasticised gel. It allows the macromolecules some freedom to move, reducing the bonding between adjacent starch molecules and reducing their crystallinity. Gelatinisation can be achieved by gently heating and shearing the starch, water and plasticiser in a conventional polymer extrusion compounding process.

The disadvantages of TPS are that it is difficult to process because of the high melt viscosity, that it has poor dimensional stability and that it develops a hydrophilic nature during ageing or so-called 'retrogradation', which leads to changes in the mechanical properties due to slow crystallisation of the material.

2.1.1.3 The role of plasticisers

A plasticiser can be defined as a chemical that reduces the stiffness of an amorphous (glassy) thermoplastic resin (Hammer, Paul & Newman, 1978). The fundamental principle associated with a plasticiser is that it interacts with the polymer chains on the molecular level and thus increases the molecular mobility of the polymer chains and decreases the glass transition temperature (T_g) of the polymer. The reduction of T_g in a polymer improves its processability.

The conditions required of a polymeric plasticiser are:

It must be compatible on a molecular scale with the polymer to be plasticised.

It must have a sufficiently low T_g so that it will efficiently lower the T_g of the polymer to be plasticised.

It must have a sufficiently high molecular weight to justify the term "polymeric" (versus oligomeric, approximately $M_n \geq 5\,000$). In addition, this implies the permanence requirements, which relate to low vapour pressure and a low diffusion rate of the plasticiser within the polymer.

When a semi-crystalline polymer is to be plasticised, the plasticiser usually forms a compatible blend with the polymer in the amorphous phase, while very little happens in the crystalline phase. However, when the degree of polymer crystallinity is very high, it could be difficult to find a plasticiser that can change the properties of the polymer.

Chapter1 (s.a.5) <http://scholar.lib.vt.edu/theses/available/etd-6998-172444/unrestricted/CHAPTER/1.PDF>, [2004, February 19].

2.1.1.4 Water and glycerol as plasticisers

The glass transition temperature (T_g) is the most important parameter in determining the mechanical properties of amorphous polymers. It can also control the rates of kinetic processes such as recrystallisation and physical ageing. The T_g of dry starch is experimentally inaccessible due to the thermal degradation of starch polymers at elevated temperatures.

The plasticisation of starch by water has been demonstrated through the decrease of the T_g of native and amorphous wheat starch and of amorphous and partially recrystallised waxy maize starch.

If water is the only plasticiser used, the resulting product is brittle when equilibrated with ambient humidity, similar to an extruded ready-to-eat breakfast cereal, whereas in the presence of other plasticisers, a rubbery material can be prepared.

Starch materials are visco-elastic and their properties are classified as a function of plasticiser content: a glassy behaviour at very low plasticiser content, a rubbery behaviour at higher plasticiser content, and gel-like behaviour at very high plasticiser content. An increase in the water and glycerol contents decreases the T_g .

Even though water was observed to be a more efficient plasticiser in the studies by Myllarinen, Partanen, Seppala & Forssell (2002), glycerol also affected the T_g . Above 20 wt% glycerol, amylose films featured much higher elongation, but were still stronger than films with a low glycerol content. Amylopectin produced very weak and non-flexible films.

Graaf, Karman & Janssen (2003) studied the glass transition temperatures in different types of starches. T_g was found to decrease in the order: T_g waxy maize > T_g wheat > T_g potato > T_g pea. With regard to the glycerol content, T_g reduces with an increase in the plasticiser in the order: T_g 15 wt%G > T_g 20 wt%G > T_g 25 wt%G. Products containing higher amounts of amylopectin (waxy maize) have higher T_g 's than materials with less

amylopectin (pea starch). The lower molecular mass of amylose and its lack of branches result in a greater free volume of pea starch so that the chains can move more easily. This explains the lower T_g of amylose compared with that of the branched amylopectin. Thus materials with a higher amylose weight fraction will have a lower T_g and will be more flexible. Glycerol has a greater impact on materials containing more amylopectin. Graaf *et al.* (2003) explain this by the fact that the T_g's of amylopectin and glycerol differ more greatly from each other than those of amylose and glycerol.

Graaf *et al.* (2003) presented plots of the DMTA (dynamic mechanical thermal analysis) curves for different types of starches. He noticed broadening of the tan δ peaks at a constant glycerol content of 15 wt% when the amylose/amylopectin ratio increases. He attributed this to increased heterogeneity with an increase in the amylose/amylopectin ratio. Hence the author suggests that an increasing of the glycerol content decreases this broadening or heterogeneity.

Using DMTA Forssell, Mikkila, Moates & Parker (1997) showed mechanical loss peaks corresponding to the glass transition of both phases: amylose and amylopectin. Amylopectin crystallisation did not occur within one week of storage in mixtures containing less than 20 wt% water. This may indicate that glycerol interacts strongly with starch, inhibiting the rate of crystallisation of amylopectin.

Glycerol containing TPS is tough and strong owing to hydrogen bonding with the starch (Van Soest & Vliegenthart, 1997). Kruger (2003) investigated the effect of plasticiser levels on the mechanical properties of TPS. He prepared samples containing Hi-Maize and a combined total of 30 wt% glycerol and water (Figure 2.3). The glycerol levels were 5, 10 or 15 wt%, with the balance being water. The lower the glycerol content, the higher are the Young's moduli of the compositions.

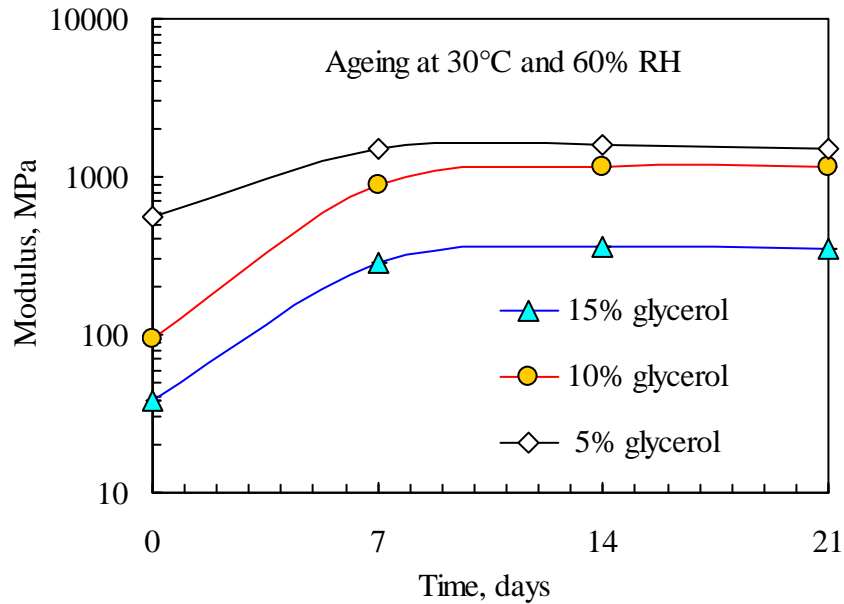


Figure 2.3: Effect of different glycerol concentrations on Young's modulus for Hi-Maize compositions, aged at 60% RH, 30°C
(Kruger, 2003)

Increasing the glycerol content extends the processing window between T_m and T_d (Liu, Yi & Feng, 2001). The increasing glycerol decreases the tensile strength, while the elongation at break increases up to a limit. Beyond this range, the elongation at break decreases with an increase in glycerol content. At high concentrations, the interactions among the molecules weaken because the insertion of glycerol reduces starch-starch macromolecular interactions. The addition of a small amount of boric acid improves the mechanical properties, especially elongation at break. Boric acid reacts with both glycerol and starch, forming a covalently bonded interconnected network (Jiugao, Songzhe, Jianping, Huawa, Jie & Tong, 1998).

2.1.1.5 Urea as plasticiser

Shogren, Swarson & Thompsons (1992) studied the structure and mechanical properties of extrudates of cornstarch with urea and glycols. They obtained flexible compositions only when enough urea and glycol was present to lower the T_g of the starch to near or below room temperature. Compositions containing high levels of urea were rather stiff, reflecting the low mobility of urea. In contrast, compositions containing

high levels of glycols were soft and weak. Samples extruded with a mixture of urea and glycols exhibited enhanced elongation at break. Urea lowers the T_g to below room temperature where the system is at thermodynamic equilibrium. Urea also disrupts starch hydrogen bonding, so no retrogradation occurs.

All samples became brittle at very low humidity and soft at high humidity. However, urea is a solid with a high melting point and little internal flexibility and hence would not be expected to add much flexibility to gelatinised starch. Since the glycols are solvents for urea, it was hypothesised that when a combination of the two was used, the urea would form a hydrogen-bonded complex with the starch which would then be solvated by the glycol. It was suspected, therefore, that this mixture might be a better plasticiser for starch than any of the others on their own. Mixtures of glycols and urea as plasticiser seem to give compositions initially having elongations (and hence toughness) greater than for similar levels of glycols alone, but they lose these with time (Shogren *et al.*, 1992; Shogren, Fanta & Doane, 1993). Tensile strength decreased and elongations increased in the order: triethylene glycol (2.4 MPa), glycerol (1.5 MPa) and propylene glycol (too soft to test).

It is interesting to carry out the reaction of starch with urea in the presence of a mineral acid or mineral acid salts. The extent of the reaction increases on the nature and concentration of the catalyst as follows: (a) sulphuric acid > nitric acid > phosphoric acid; and (b) ammonium sulphate > ammonium nitrate > ammonium chloride > magnesium sulphate. Khalil, Farag, Alt & Hebeish (2002) suggested that the acid performs two main functions. Firstly, it prevents cross-linking. Secondly, it degrades starch molecules via hydrolysis, thereby lowering the molecular size of the starch and thus enhancing its solubility.

Other plasticisers include sucrose, glucose, xylose and fructose. Kalichevsky, Jaroszkiwicz, Abllet, Blanshard & Lillford (1992) studied the effect of fructose and water mixtures on the dynamic mechanical properties of waxy maize. Two glass

transitions were detected and fructose had a greater plasticising effect at low water content (Forssell *et al.*, 1997).

2.1.1.6 Crystallization, ageing and mechanical properties of TPS in relation to changes in B-type crystallinity

Starch is semi-crystalline, with a crystallinity of 20 – 45%. Native starch has a high degree of supermolecular organisation within the granules. The amylopectin molecules are organised in a radial pattern. Amylose and the branching points of amylopectin form amorphous regions in the starch granules. Amylopectin is the main crystalline component in granular starch. The crystalline regions, consisting of double helices of the amylopectin outer chains, are arranged as thin lamellar domains. Additional crystallinity may arise from co-crystallisation with amylose and from amylose crystallisation into single-helical structures, which form complexes with fatty acids or lipids (Van Soest & Vliegenhart, 1997; Zobel, 1988).

Several types of crystal structure are observed in the granules, denoted V-, A-, or B-type, which differ in the packaging density of the single or double helices and in water content. Starches are labelled according to the type of crystallite present in the granules. Most cereal starches give A pattern; potato and other root starches give B pattern (Hoseney, 1994; Rao & Hartel, 1998). Hence cereal and potato are termed A-type and B-type. Starches such as pea, which contain both A- and B-crystallites, are termed C-type. The relative abundances of the crystal structure are influenced by the amylose/amylopectin ratio, molecular mass, degree of branching and length of the amylopectin outer chains.

Processing-induced crystallisation of amylose:

Crystal structures have characteristic X-ray diffraction patterns, owing to differences in the crystal lattice and the degree of hydration. The processing parameters, amylose content and additives mainly determine the formation of single helices. During processing, an increase in the input of mechanical energy, which is related to the extrusion screw speed or the processing time during kneading, causes an increase of

the amount of single-helix-type crystallinity (Van Soest & Vliegenthart, 1997). Due to high shear conditions the starch granules are molten or physically broken up into small fragments and therefore no bi-refringence is observed (Van Soest, Hulleman, De Wit & Vliegenthart, 1996a). Neat starch granules show bi-refringence, i.e. it rotates a plane of polarised light to producing interference crosses. These are characteristic for each starch type and it is one of the features used in identifying a starch source. When the radial orientation of a crystalline micelle is disturbed, the bi-refringent cross disappears (The Starch Granule (s.a.8) <http://www.eco-foam.com/processing.asp>, [2004, February 19]).

Processing-induced crystallisation of amylose is caused by the rapid recrystallisation of single-helical structures of amylose during cooling after processing. Three types of crystallinity have been observed in this situation, and identified as VH-, VA -, and EH-type crystals. Thus Van Soest *et al.* (1996a) divide crystallinity as found in the starch into A-, B- and C-type due to incomplete melting during processing, and into V- or E-type due to processing-induced amylose crystallisation.

The presence of isophospholipids and complex-forming agents also induces amylose crystallisation. Complex-forming agents, such as isopropanol, show a strong interaction with starch and are incorporated into the amylose crystals.

The amount of crystallised amylose is proportional to the amylose content, and in waxy starch materials, which contain little or no amylose, no single-helix-type crystallinity is observed. The relative amounts of the various amylose single-helical structures and the rate of change are determined by temperatures and humidity (Van Soest & Vliegenthart, 1997).

Crystallisation during storage:

In glycerol-containing starch plastics, both amylose and amylopectin recrystallise in the B-type crystal structure. During storage structural changes occur. First, double helices and aggregates of double helices (short-range ordering) are formed and then

crystallisation (long-range ordering) occurs. The crystallisation rate is influenced by the amylose content, starch source and storage conditions. Amylose crystallisation is fast compared with that of the amylopectin outer chains, which can be either intramolecular or intermolecular.

Golding (1998) suggests that the annealing temperature may have an effect on crystallisation. Jasberg & Shogren (1994) aged high-amylose starch at various temperatures. They classified the ageing below the T_g as physical ageing, which they found resulted in no change of crystallinity. Above the T_g the ageing was classified as retrogradation, which brings about structural changes and crystallisation.

The intramolecular amylopectin B-crystallisation weakens the materials by inducing internal stresses and reducing the intermolecular interactions, thus explaining the observed deterioration of starch plastics during storage. Hizukuri, quoted by van Soest (1996a) proposed that the amylopectin molecules tend to form a more compact cluster structure, which during ageing according to Hammer *et al.*, (1978) results in an increased internal stress in the TPS materials. Spontaneous cracks are formed at the crystalline junction zones.

The intermolecular B-crystallisation of both amylopectin-amylopectin and amylose-amylopectin increases the strength and stiffness of the materials because of physical cross-linking of the amorphous amylose and amylopectin.

The aggregation and crystallisation of helices between adjacent amylopectin molecules is less effective in reinforcing the matrix than the aggregation and crystallisation of amylose molecules, because the shorter length of the amylopectin outer chains results in smaller interaction domains (Hammer *et al.*, 1978).

During ageing, the plasticiser content of starch plastics affects the rate of crystallisation. Higher amounts of plasticiser cause an increase in the mobility of the starch chains and lower T_g 's.

The rate of crystallisation increases with increasing water content. Jang & Pyun (1997) examined the effect of moisture level on the crystallinity of wheat starch aged at different temperatures. They concluded that the optimum temperature for crystallisation was $T = (T_g + T_m)/2$.

Conversely, glycerol reduces the crystallisation rate at constant water content owing to the starch-glycerol interaction and a reduction in both starch mobility and water stabilisation. However, due to the hygroscopicity of glycerol, the water content usually increases, thereby lowering T_g and increasing the crystallisation rate (Van Soest and Vliegthart, 1997).

Brittleness:

One of the main problems with starch materials is their brittleness. When stored, the brittleness even increases due to the retrogradation and volume-relaxation processes. During retrogradation and volume relaxation, part of the starch recrystallises. This process can be divided into two parts. The recrystallisation of the amylose component is an irreversible and very fast process. However, the reversible crystallisation of amylopectin is slower. So the retrogradation can be referred to as the long-term recrystallisation of the amylopectin component (Graaf *et al.*, 2003).

Crystallisation – stress-strain:

The influence of crystallisation on the stress-strain behaviour of thermoplastic potato starch was monitored by Van Soest and co-workers (1996a,b,c). The materials were stored for an initial storage period of two weeks at 60% RH and 20°C. After this initial period they were stored for two weeks at various relative humidities, namely 55, 60, 70 and 90% RH, to obtain information about the dependence of the properties on storage humidity. Subsequently, all materials were reconditioned at $60 \pm 5\%$ RH for two weeks to level out the differences in water content after storage at different RH's, after which mechanical testing and XRD were performed. Directly, within a few hours after extrusion, a small amount of EH-type crystallinity is formed, which is metastable and

rearranges during storage for more than several days at 60% RH into a six-fold helical crystal structure, labelled as VH (H-hydrated). These types of structure are formed by the crystallisation of amylose.

TPS material, stored at 55% RH, has a T_g of 35 ± 5°C, which is above storage temperature. No B-type crystallinity is observed in these materials. Materials stored at 60% RH show only a slight increase in B-type crystallinity after the initial storage period of two weeks. The E-modulus and tensile strength are slightly increased, while the elongation at break decreases. The properties change drastically at 70% RH and even more at 90% RH. The B-type crystallinity increases as well with the time. The E-modulus and tensile strength increase with an increase in the RH, while the elongation at break decreases when TPS is aged for two weeks. The percentage crystallinity increases with an increase in the RH (Van Soest *et al.*, 1996a,b,c).

Shrinkage:

The samples made by *injection moulding* change in size during storage. In the injection direction there is an obvious shrinkage and in the direction perpendicular to it (the width), an increase of size is detectable. During the injection moulding the polymer in the mould experiences elongational flow and consequently the chains of the polymers are orientated in the injection direction. Therefore the chains are in a stretched conformation and lie parallel to each other. When the injection is stopped, reorientation starts and the chains realign in a helix configuration. This explains the shrinkage in the injection direction and the swelling in the width. Besides that, retrogradation will also cause shrinkage by the forming of hydrogen bonds between the chains, with repulsion of water molecules.

As expected, shrinkage takes place faster at increasing glycerol fraction. This is due to a decrease in the local viscosity and an increase in the mobility of the chains, which makes a faster relaxation possible.

The shrinkage of waxy maize takes much more time than that of other starches. The large amount of amylopectin makes the chains more entangled, which causes many interactions and limited freedom to move compared with starch with higher amylose content (Graaf *et al.*, 2003).

2.1.1.7 The Role of lubricants

Lubricants are substances that help in the processing of plastics. They improve flow properties and reduce the adherence of the melt to machine parts. Thermoplastic materials have high molecular weight and their melts are highly viscous. Lowering of the melt viscosity of the material can be achieved by increasing the processing temperatures or by the use of lubricants, which decrease the internal and external friction of the melt with the machine parts. Increasing the processing temperature has limitations since above specific temperatures, the material starts to depolymerise and loses its strength.

Lubricants coat the surface of the polymer particles, helping them to flow more easily in the colder parts of the processing machine. With an increase in temperature, the lubricant melts and penetrates the polymer. The rate of penetration is dependent on the solubility of the polymer. The solubility of the lubricant depends on its structure and polarity in relation to that of the polymer (Ritchie, 1972).

2.1.1.8 Blends

Starch is highly hydrophilic and starch-based components disintegrate readily on contact with water. These problems can be overcome through chemical modification as the starch has free hydroxyl groups which readily undergo a number of reactions such as acetylation, esterification and etherification (Nolan-ITU, 2002; African Products, s.a.1).

Another way of improving the processability of the TPS is to use polymer blends. Along with the ongoing search for new materials, modifications of existing polymers by blending have shown promise in economically tailoring materials to have desirable

properties. Ideally, two or more polymers may be blended together to form products that show desirable combinations of properties. However, most of the polymer pairs are not thermodynamically miscible and so exist in two different phases. This separation into two phases creates an interface, which might lead to poor performance of the blend system. A typical case of high interfacial tension and poor adhesion between the two phases leads to a lower degree of dispersion and to gross separation during later processing or use. Poor adhesion hinders the formation of highly structured morphologies. It also leads to very weak and brittle mechanical properties due to poor stress transfer between phases (Paul & Newman, 1978).

Polymer multi-component systems are categorised as follows: (a) polymer blends, (b) copolymers and (c) reinforced composites. Better dispersion can be expected in the case of a copolymerisation, where a chemical bond is present, than in a blend system consisting of same polymer pairs. Still, it has been observed that nearly all copolymers exhibit some degree of phase separation (Kollinsky & Markert, 1971). Thus to define the interaction between the polymer pairs at the molecular level, the term 'compatibility' has been used in the technical literature. However, compatibility is not synonymous with miscibility since it is used to characterise the relative ease of fabrication or performance of the two polymers in a blend. Blend components that can resist gross phase segregation and/or show desirable blend properties are said to possess some degree of compatibility, though they may not be miscible at all from a thermodynamic point of view (Paul & Newman, 1978).

Blends of biodegradable synthetic aliphatic polyesters and starch are often used to produce high-quality sheets and films for packaging by flat-film extrusion using chill-roll casting or by blown film methods since it is difficult to cast films from 100% starch in a melted state. Around 50 wt% of the synthetic polyester at US\$4 – 5.00/kg can be replaced with natural polymers such as starch at US\$1.50/kg, leading to a significant reduction in cost. Another advantage is that the polyesters can be modified by incorporating a functional group capable of reacting with starch polymers (Nolan-ITU, 2002).

Biodegradable polyesters are expensive. Starch is also not fully compatible with these polyesters. In order to retain processability, water resistance and desirable properties, less than 50 wt% of starch is used. The starch blends therefore remain expensive and have only found niche-market applications.

Polyvinyl butyral (PVB) is used in the manufacture of safety glass, in 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 wt% PVB, with 30 to 45 wt% plasticiser. Large quantities of PVB are recovered from scrap windscreens, but there is very little interest in recycling this waste due to contamination with glass. Consequently, it is disposed of in landfill or incinerated (Sita, Burns, Häßler & Focke, 2006)

Chen, David, Mac Knight and Karasz (2001) investigated the miscibility and morphology of blends of biodegradable poly(3-hydroxybutyrate)(PHB) and poly(vinyl butyral)PVB by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). PHB has semicrystalline structure. PVB contains vinyl butyral (VB) and vinyl alcohol (VA). DSC shows two Tg's, indicating immiscibility. However, partial miscibility is observed in 50/50 (w/w) blends, containing PVB with 25-36 wt% VA content.

Interesting is the invention of Buhler, Schmid and Schultze (1995), describing highly transparent, single-phase, biodegradable starch mixture, consisting of selected biodegradable polyamides and starch, having an amylose content of 50 wt%. The composition contains emulsifiers, urea and chemically modified starch and plasticizer. No polymeric compatibilizer has been involved. Preferred polyamides are based on caprolactam, lauro lactam, ω – aminocaproic acid, hexamethylene diamine with adipic acid.

2.1.1.9 Compatibility of the blends

To increase the compatibility between two phases of a blend, a compatibiliser could be used. These are usually copolymers, which are compatible with the two phases in the blend system.

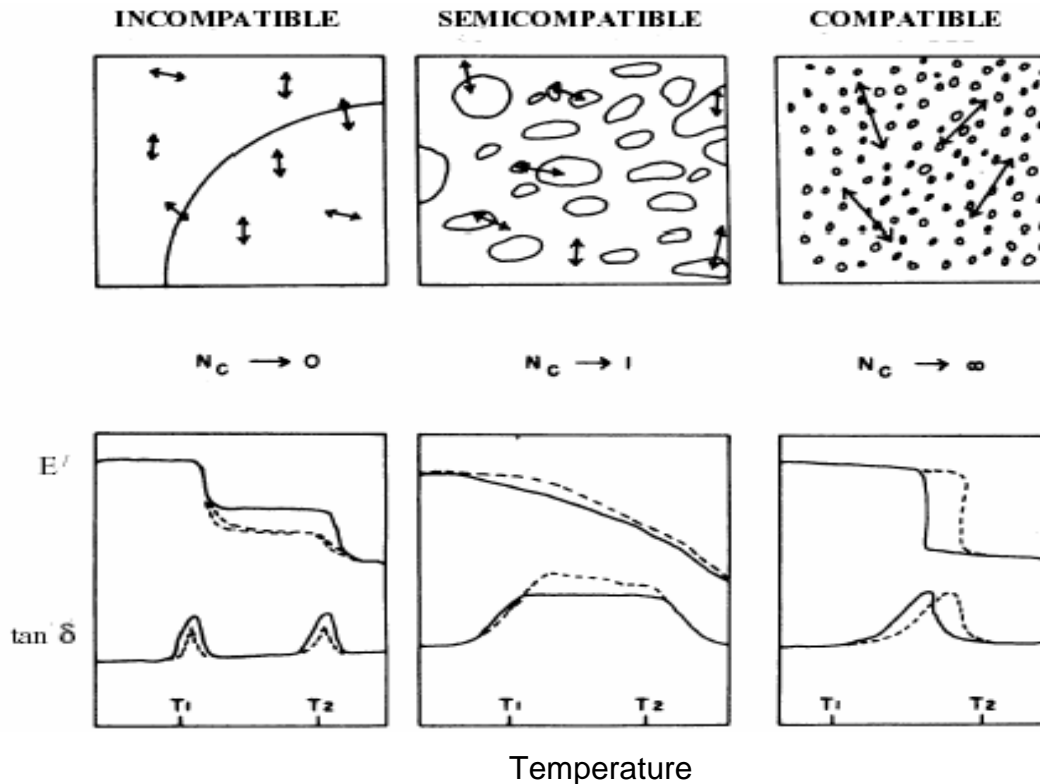


Figure 2.4: Compatibility of blends (Kaplan, 1976)

Figure 2.4 is a representation of a two-phase system, which illustrates compatible, incompatible and semi-compatible systems by using DMS. Heterogeneous systems can be defined as compatible, although they show a large degree of phase separation and two distinct glass transitions. The compatibility or homogeneity of a polymer blend can be defined in terms of the dimensions of the separate phases using different measurement techniques. These are differential scanning calorimetry (DSC), dynamic mechanical spectra (DMS), thermo-mechanical analysis (TMA), and nuclear magnetic resonance (NMR). (Kaplan, 1976) defines compatibility by a compatibility number:

$$N_c = \frac{\text{Experimental Probe Size}}{\text{Domain Sizes of Phases}}$$

The experimental probe size is defined as the scale of resolution of an instrumental technique. The domain size is the average dimension of the dispersed phase in the polymer blend (See Figure 2.4).

Thus, when $N_c \rightarrow \infty$ the system is compatible

when $N_c \rightarrow 1$, the system is semi-compatible

when $N_c \rightarrow 0$, the system is incompatible.

When N_c approaches zero, the dimension of each existing phase is much greater than the probe size of the instrument. The instrument detects two transitions, corresponding to each phase. Two distinct T_g 's are observed.

When $N_c \rightarrow \infty$, the probe size is much greater than the phase dimensions. The instrument reports a single T_g ,

For the semi-compatible case, the $\tan \delta$ curve damping is much broader, corresponding to a plateau. The detection of a single or double transition in a two-phase system by a DMS instrument gives an indication of the dimensions of the phases present in the system. The dimension that corresponds to a dynamic mechanical thermal analysis is approximately 15 nm. The NMR technique, can detect in the dimensional range of 2.5 to 5 nm.

Chapter1 (s.a.5) <http://scholar.lib.vt.edu/theses/available/etd-6998-172444/unrestricted/CHAPTER/1.PDF>, [2004, February 19].

2.1.2 Polyester compositions for golf tees applications

Polyesters play a predominant role as biodegradable plastics due to their hydrolysable ester bonds. The polyester family is made up of two major groups – aliphatic (linear) polyesters and aromatic (aromatic rings) polyesters (Figure 2.5).

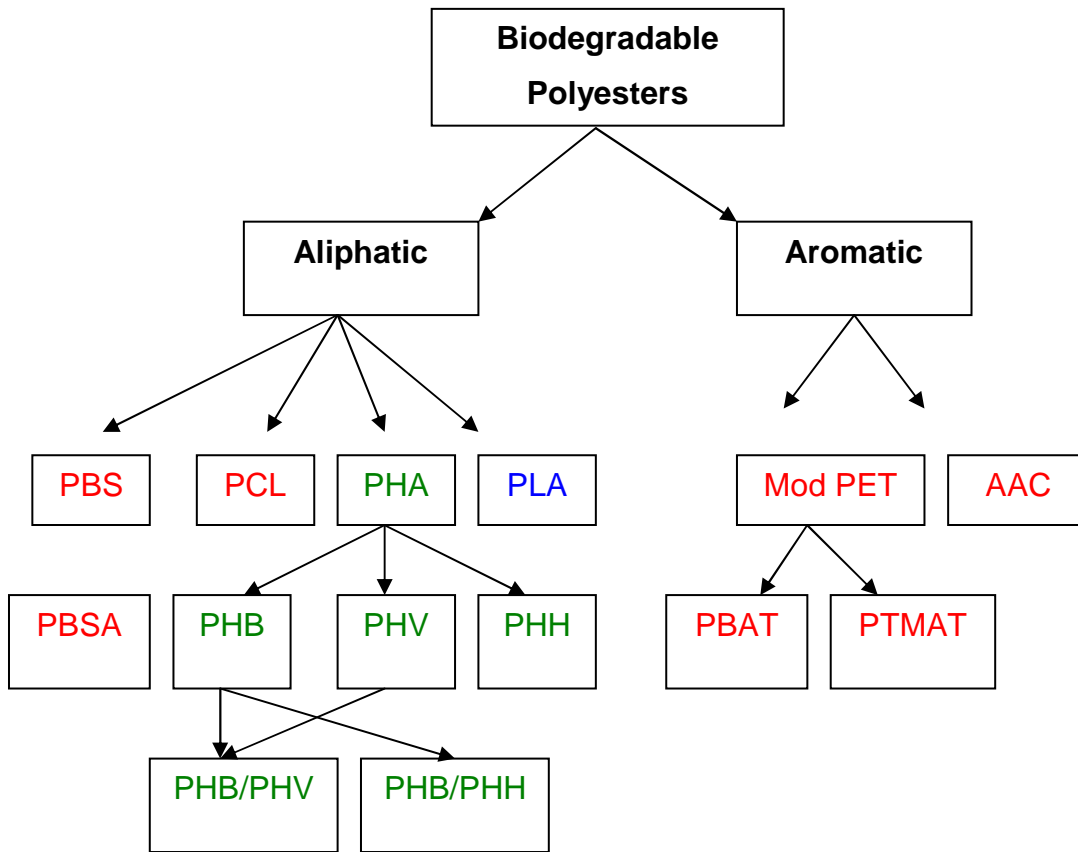


Figure 2.5: Biodegradable polyesters family

PHA = polyhydroxyalkanoates, PHB = polyhydroxybutyrate

PHH = polyhydroxyhexanoate, PHV = polyhydroxyvalerate

PLA - polylactic acid, PCL = polycaprolactone

PBS = polybutylene succinate, PBSA = polybutylene succinate adipate

AAC = aliphatic-aromatic copolyesters, Mod PET = modified polyethylene terephthalate

PBAT = polybutylene adipate/terephthalate

PTMAT = polymethylene adipate/terephthalate

Naturally produced – Renewable; Synthetic – Renewable; Synthetic – Non-renewable

Aromatic polyesters have excellent material properties, but they are very resistant to microbial attack. Aliphatic polyesters, on the other side, are biodegradable, but lack good mechanical properties. Aliphatic polyesters have better moisture resistance than starches, which have many hydroxyl groups. These aliphatic polyesters are much more expensive and lack mechanical strength compared with conventional plastics such as polyethylene. All polyesters degrade, with hydrolysis being the main mechanism.

Synthetic aliphatic polyesters are synthesised from diols and dicarboxylic acids via condensation polymerisation, and are known to be completely biodegradable in soil and water. As mentioned earlier, these polyesters are blended with starch-based polymers for cost reduction. Hoshino, Sawada, Yokota, Tsuiji, Fukuda & Kimura (2001) measured the rate of soil degradation of poly-(3-hydroxy-butyrate-valerate) (PHB/PHV), PCL, PBS, PBSA and PLA during soil burial for 12 months. Samples were collected every three months for measurement of weight loss. The rate of degradation of PBSA, PHB/PHV and PCL was found to be similar. The degradation rate of PBS and PLA was found to be slower (Nolan-ITU, 2002).

2.2.2.1 PHA polyesters (Biodegradable Polyesters: Packaging goes green (s.a.4)
<http://www.plasticstechnology.com/articles/200209fa3.html>, [2004, June 06]
(Nolan-ITU, 2002)

Polyhydroxyalkanoates (PHAs) are the major group of naturally produced aliphatic polyesters. The two main members of the PHA family are polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV). Such polymers are actually synthesised by microbes, with the polymer accumulating in the microbes' cells during growth. The PHB homopolymer is a stiff, brittle polymer with high crystallinity and mechanical properties like those of polystyrene, but it is less brittle. PHB copolymers are preferred for general purposes as the degradation rate of PHB homopolymer is high at its normal melt-processing temperature.

The common commercial PHA consists of a copolymer, PHB/PHV, together with a plasticiser and inorganic fillers such as titanium dioxide and calcium carbonate. PHB

and its copolymers with PHV can be melt-processed much more easily. They are fully biodegradable and suited to applications with short usage and high degradation rate requirements. The products of this degradation are non-toxic. The applications of PHA are blow- and injection-moulded bottles and films.

Goodbole, Gote, Latkar & Chakrabarti (2003) studied the properties of PHB blended with starch. The blend films had a single glass transition temperature for all the proportions tested. The nature of the blends was found to be crystalline. The tensile strength was optimum for the PHB:starch ratio of 0.7:0.3(wt/wt).

Shin, Kim & Kim (1997) found that bacterial PHB/PHV (92/8 w/w) was degraded nearly to completion within 20 days of cultivation by anaerobic digested sludge, while synthetic aliphatic polyesters such as PLA, PBS and PBSA did not degrade at all in 100 days. PHB/PHV exhibited a similar degradation behaviour to cellophane, which was used as a control material.

Under simulated landfill conditions, PHB/PHV degraded within six months. Synthetic aliphatic polyesters also showed significant weight losses through one year of cultivation (Purushothaman, Anderson, Narayana & Jayaraman, 2001).

The commercial candidates from this group are Biopol PHBV, developed by Metabolix, and Nodax PHBV, marketed by Procter & Gamble. The crystallinity of PHAs can be manipulated to match the performance of engineered thermoplastics.

2.2.2.2 PLA (renewable) polyesters (Nolan-ITU, 2002)

Polylactic acid (PLA) is a linear aliphatic polyester produced by poly-condensation of naturally produced lactic acid or by the catalytic ring-opening of the lactide group. Lactic acid is produced via starch fermentation. The ester linkages in PLA are sensitive to both hydrolysis and enzymatic activity.

PLA is often blended with starch to increase biodegradability and reduce costs. The brittleness of the starch-PLA blend can be corrected using plasticisers such as glycerol, sorbitol and triethyl citrate, which reduce this effect. PLA is fully biodegradable when composted at temperatures of 60°C and above. The first two weeks of degradation of PLA is via hydrolysis to water-soluble compounds and lactic acid. Rapid metabolisation of these products into CO₂, water and biomass by a variety of microorganisms occurs after hydrolysis, causing weight loss and formation of a porous structure. Increased hydrolysis takes place in an alkaline environment, in contrast to other biopolymer materials. The enzymes causing the degradation are pronase, proteinase K, ficin, esterase and trypsin. PLA does not biodegrade at temperatures lower than 60°C due to its glass transition temperature being close to 60°C (Nolan-ITU, 2002) (Shimao, 2001). Grafting of the PLA chains with maleic anhydride through free radical reaction conducted by reactive extrusion improves the poor mechanical performances of PLA/starch compositions (Dubois and Narayan, 2002).

2.2.2.3 PCL and PBS (synthetic aliphatic) polyesters

Polycaprolactone (PCL) is a biodegradable synthetic aliphatic polyester. It is made by the ring-opening polymerisation of caprolactone. It has a low melting point, low viscosity and good processability. PCL is fully biodegradable when composted. The low melting point of PCL makes the material suitable for composting due to the temperatures obtained during composting exceeding 60°C. The biological degradation is done by fungi; the rate of hydrolysis depends on its mole mass and crystallinity. Chemical hydrolysis occurs more slowly than with PLA. PCL was previously not widely used due to cost reasons, which have been overcome by blending the polymer with cornstarch (Shimao, 2001). Blends containing up to 45 wt% starch and PCL can be biodegradable. However, this material is not strong enough for most applications as the melting onset temperature is only 60°C. It actually softens at temperatures above 40°C. These drawbacks limit the applications of the starch-PCL blends.

Rutkowska, Krasowska, Heimovska, Smiechowska & Janik (2000) studied the influence of different processing additives on the biodegradation of PCL film in compost with

activated sludge. They found that PCL without additives completely degraded after six weeks in compost with activated sludge. The introduction of processing additives gave the materials better tensile strength but made them less vulnerable to microorganism attack (Nolan-ITU, 2002; Janik, Justrebska & Rutkowska, 1998; Rutkowska *et al.*, 2000). An improvement of the mechanical properties and interfacial adhesion between PCL/starch is reported by Dubois and Narayan (2002). The compatibilization was achieved via grafting PCL chains onto a polysaccharide backbone using dextran. The compatibilized composition displayed much more rapid biodegradation measured by composting testing.

Polybutylene succinate (PBS) is a biodegradable synthetic aliphatic polyester with similar properties to PET. PBS is generally blended with other compounds, such as starch (TPS) and adipate copolymers, to form PBSA. It has excellent mechanical properties and can be easily processed via conventional melt techniques. In Japan it is produced under the name of Bionelle by Showa Highpolymer. In Korea the name is Sky Green BDP and the producer is SK Polymers. In the USA the Bionelle products are used in commodity tubes, agricultural films, traffic cones and industrial trays. Some grades are modified with diisocyanate chain extenders to improve the stiffness and thermal properties. SK Chemicals Sky Green BDP products offer LDPE-like properties. They are used in films, disposable cutlery, food tubes, hairbrush handles and paper coatings. Aliphatic versions biodegrade more rapidly and offer better processing and tensile properties than the aromatic-aliphatic grades, which cost less.

(Biodegradable Polyesters: Packaging goes green (s.a.4)

<http://www.plasticstechnology.com/articles/200209fa3.html>, [2004, June 07]).

PBS biodegrades via a hydrolysis mechanism. Hydrolysis occurs at the ester linkages and this results in a lowering of the polymer's molecular weight, allowing for further degradation by micro-organisms. SK Chemicals (Korea), a leading manufacturer of PBS polymers, quotes a degradation rate of one month for 50% degradation for 40 micron-thick film in garden soil (Nolan-ITU, 2002). To improve the phase stability of PBS/A - starch blends a small amount (5% by weight) of compatibiliser (maleic anhydride

functionalised polyester) can be added. At a higher starch content (>60 wt%), such sheets can become brittle, which can be overcome by the addition of a plasticiser, making them more flexible. Ratto, Stenhouse, Auerbach, Mitchell & Farrell (1999) investigated the properties of PBSA and cornstarch blends. PBSA is biodegradable and exhibits excellent thermoplastic properties. The aim of the study was to obtain a mixture that maximised these properties while minimising cost. Cornstarch was blended with PBSA at concentrations of 5 – 30 wt% by weight. The tensile strength of the blends was lower than that of the polyester alone, but there was not a significant drop in strength with increasing starch content. The melt temperature and processing properties were not affected by the starch content.

The blends of PBSA and cornstarch were investigated for biodegradability by measuring CO₂ production in a soil burial test. Even a 5 wt% starch addition showed a large reduction in the half-life from that of the pure polyester. The half-life was found to decline with increasing starch content until a minimum at about 20 wt% starch content was reached (Nolan-ITU, 2002; Ratto *et al.*, 1999).

Lim, Jung & Jin (1999) studied the properties of an aliphatic polyester blended with wheat starch. The polyester was synthesised from the poly-condensation of 1,4-butanediol and a mixture of adipic and succinic acids. The wheat starch-polyester blends were found to have melting points near that of the polyester alone. The addition of a plasticiser made the blends more flexible and processable than the polyester itself. The plasticised blends retained a high tensile strength and elongation at the break, even at high concentrations of starch. The wheat starch-aliphatic polyester blend studied by Lim *et al.* (1999) demonstrated excellent biodegradability. Soil burial tests revealed complete biodegradation within eight weeks. All these properties make the blends ideal as commodity biodegradable plastics.

2.2.2.4 Aliphatic-aromatic copolyesters(AAC) and Modified PET (Biodegradable Polyesters: Packaging goes green (s.a.4); (Nolan-ITU, 2002)

<http://www.plasticstechnology.com/articles/200209fa3.html>, [2004, June 07]

Aliphatic-aromatic copolyesters have the biodegradable properties of aliphatic polyesters with the mechanical properties of aromatic polyesters. For reduction of their cost, AACs are often blended with TPS.

The properties of AACs, such as transparency, flexibility and anti-fogging performance, are very close to those of the blow moulding low-density polyethylene. They meet the requirements for film used in food wrapping of fruit and vegetables, with the advantage of being compostable.

The rate of the biodegradation in soil or compost can be influenced by the composition of the copolyester, moisture content, temperature, surface area and the method used to manufacture the finished product. In an active microbial environment, the polymer becomes invisible within 12 weeks. Commercial members of the family are Ecoflex F from BASF AG and Eastar Bio Copolyester 14766 from Eastman Chemicals. These copolyesters are based on butanediol, adipic acid and terephthalic acid. The Eastman version is highly linear in structure, whereas BASF's products have long-chain branching.

Modified PET contains comonomers introducing ether, ester or amide groups. They provide 'weak' linkages, susceptible to biodegradation via hydrolysis and following enzymatic attack on these bonds. The modified PET materials include PBAT (polybutylene adipate/terephthalate) and PTMAT (polytetramethylene adipate/terephthalate). Specifically modified polymer can be created for a specific biodegradable application, varying the comonomers used. In the semi-crystalline category, Du Pont offers modified PET incorporating three different aliphatic monomers. Biomax 6962 has a 1.35 g/cc density and a melting point of 195°C versus 250°C for PET. The mechanical properties include high stiffness and can vary in elongation. Dupont has targeted fast-food disposable packaging, waste tubes, agricultural film, flower pots and bottles.

3 EXPERIMENTAL DETAILS

3.1 MATERIALS

Table 3.1: Raw materials and producers/suppliers

Raw material	Grade	Supplier/Producer
Starch	Hi-Maize	African Products
Dimer acid polyamides	Euremelt 2138	Vantico AG/Supplier Huntsman Advanced Materials/Producer
Linear polyamide copolymer	Grilon BM 13 SBG Natur	EMS
Polyvinylbutyral (PVB)	Recycled material	Vest Design Seven
Poly (ethylene-co-vinyl acetate)	Elvax 210	Du Pont
Glycerol	*CP	Crest Chemicals
Polybutylene succinate adipate (PBSA)	SGPE/ (film grade)	SK Chemicals (Korea)
Urea	*CP	Obaru
Stearic acid	*CP	Protea Industrial Chemicals
Stearic alcohol	*CP	Protea Industrial Chemicals
Precipitated silica	Vulcasil S	Bayer

* CP = chemically pure

3.2 APPARATUS

Mixing:

A mixer was used for the mixing of the starch and the plasticiser. Figure 3.1 shows the high-speed Papenmeier mixer used.

Procedure:

- Mix the starch and stearyl alcohol in a Papenmeier (TGHK 63) high-speed mixer.
- Slowly add water and glycerol to the mixture. The temperature should not exceed 65°C.
- Mix for 20 minutes at the slow speed (ca. 1 200 r/min).
- Cool down to ambient temperature.
- Add the silica and mix for 1 minute.



Figure 3.1: Papenmeier mixer (K model)

Extrusion:

Starch mixes were gelled using a 25 mm single-screw laboratory extruder with an L/D ratio of 25 (Figure 3.2). The conditioned TPS granules were used to prepare blends with PVB and polyamides in the same laboratory extruder. The temperature profile along the barrel was 105 – 120°C at the feed section, 110 – 145°C at the compression and metering zones and ca. 100°C at the die zone. The higher temperatures were required for blends containing higher amounts of starch.



Figure 3.2: CTM extruder

A Berstorff extruder with co-rotating double screws and diameter of 40mm was used for the preparation of the polyester/starch blend.

Injection moulding:

Tensile test specimens, conforming to ASTM D638, were injection-moulded using an Engel 3040 machine (Figure 3.3) with an 800 kN clamping force. It was necessary to optimise the injection moulder settings for each formulation in order to ensure flash-free mould filling without damaging the parts. Typical barrel temperatures, from the feeding zone to the nozzle, were: 100 – 120°C, 120 – 150°C, 120 – 150°C and 100 – 120°C.



Figure 3.3: Injection moulder Engel 3040, 800 kN

Moisture analysis:

Moisture analyser model: Mettler LP16 balance was used for determining the moisture in the specimens.

Humidity cupboard:

- The samples were aged in a Labcon Humidity Cupboard at 60% RH and 30°C.
- For low relative humidity, desiccators filled with P₂O₅ were used.
- For the compostability tests, a Labcon Humidity Cupboard at 60% RH, 30°C was used

X-Ray Diffraction (XRD):

An automated Siemens diffractometer was used (Table 3.2).

Table 3.2: Settings of the Siemens D-501 automated diffractometer

Instrument	Siemens D-501
Radiation	Cu K α (1.542 Å)
Temperature	25°C
Specimen	Flat-plate, rotating (30 r/min)
Power Settings	40 kV, 40 mA
Soller slits	2° (diffracted beam side)
Divergence slits	1°
Receiving slits	0.05°
Monochromator	Secondary, graphite
Detector	Scintillation counter
Range of 2 θ	5-70°2 θ
Step width	0.04°2 θ
Time per step	1.5 s

Scanning Electron Microscope (SEM):

Low magnification scanning electron microscopy (SEM) images of gold-coated samples of the fracture surfaces were obtained on a JEOL 840 SEM.

3.3 TEST METHODS

The main international organisations that have established standards for biodegradation are:

- American Society for Testing and Materials (ASTM)
- European Standardization Committee (CEN)
- International Standards Organization (ISO)
- Institute of Standards Research (ISR)
- German Institute for Standardization (DIN)
- Organic Reclamation and Composting Association (ORCA) (Belgium) (Phillips, 1998; Technical committee standards list (s.a.9)

<http://www.iso.ch/iso/en/stddevelopment/tc/tclist>, [2004, March 4].

3.3.1 Tensile testing

Standards for the tensile properties of plastics:

- ASTM D 638
- DIN 53441
- DIN 53444
- DIN 53452 (Phillips, 1998; Technical committee standards list (s.a.8)

<http://www.iso.ch/iso/en/stddevelopment/tc/tclist>, 2004, March 4).

The test method used in this evaluation was ASTM D 638. The tensile testing was done for two different conditions of aged samples: 0% RH , ambient temperature, and 60% RH , 30°C. The tensile tests were performed at a speed of 50 mm/min on a Lloyd machine.

The tensile strength, elastic modulus and work-to-break give an indication of the brittleness of the composition, but this is best evaluated from the elongation at break (strain) of the specimen.

Tensile testing is a common technique used to determine the mechanical properties of materials. In this case the aspects of importance were:

Tensile stress:

$$\sigma = \frac{F}{A_o}$$

Where σ = tensile stress in Pa

F = tensile force in N

A_o = the original cross-section (of the unloaded specimen) in m².

Strain (elongation at break):

$$\varepsilon = \frac{\Delta l}{l_o}$$

Where ε = elongation at break

l_o = original length (of the unloaded specimen) in m

Δl = change in length of the loaded specimen at failure.

Modulus of elasticity:

Hooke's law provides the simplest relationship between stress and strain:

$$\sigma = E\varepsilon$$

E is known as "Young's modulus"

The graphs of the TPS and TPS blends do not show the presence of yield stress, which is the onset of plastic deformation, typical of most conventional plastics (Figure 3.4).

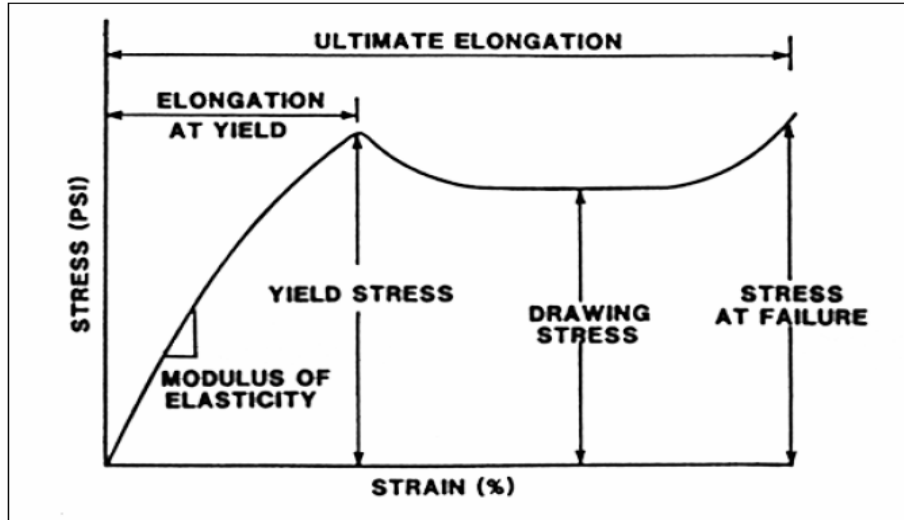


Figure 3.4: Stress-strain curve for traditional semi-crystalline thermoplastics
(Cheremisinoff, 1993)

In contrast to traditional plastics, starch plastics have only continual plastic deformation prior to failure, with no region of elastic deformation (Figure 3.5: Meadows, 1998).

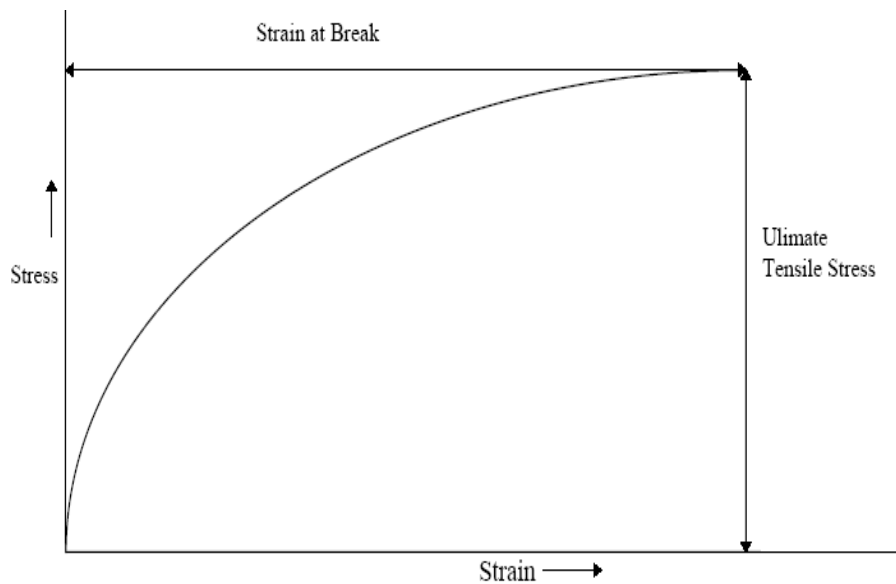


Figure 3.5: Stress-strain curve for thermoplastic starch (TPS)
(Meadows, 1998)

3.3.2 X-ray diffraction (XRD) analysis

The diffraction of X-rays by matter is a method that has been applied to crystalline materials. X-rays can be described as waves of electromagnetic radiation of short wavelengths and high energy. The range is from 10^{-4} nm to 10 nm. The X-rays used in diffraction are in the region of 0.05 to 0.25 nm (visible light = 600 nm) (Skoog & Leary, 1992).

When X-rays interact with the matter they are scattered. In a crystal, the scattering centres or atoms are located at fixed distances and distributed in a regular way. The diffraction angles (θ) are related to the interplanar distance of the crystal sheets. When we use an X-ray with a known wavelength and have the angle of the incident beam θ , then d (the distance between successive planes), can be determined by the Bragg's equation:

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

Where θ = the angle of the incident beam with the crystal surface

n = an integer

λ = the wavelength of the incoming X-ray

d = the interplanar distance in the crystal, which is characteristic for each crystal matter (Skoog & Leary, 1992; Jenkins, Gould & Gedcke, 1981; Williams, 1987).

3.3.3 Compostability

Standards for the compostability of plastics (see Table 3.3) include:

- ASTM G-160
- ASTM D-5338
- ISO 846
- ISO 14855
- ISO 14852

- CEN 13432
- DIN V 54 900

(ASTM D 5338, 1992; ISO 846, 1978; ASTM G 160, 1998; ASTM G 160 (s.a.3), <http://www.astm.org>, [2004, March 4].

The ASTM defines biodegradable as "capable of undergoing degradation into carbon dioxide, methane, water, inorganic compounds or biomass in which the predominant mechanism is the enzymatic action of microorganisms, which can be measured by standardized tests in a specified period of time, reflecting available disposal conditions" It is important that the time limit be specified.

A polymer is 'compostable', when it is biodegradable under composting conditions or conditions in which:

The polymer chains break down under the action of microorganisms (bacteria, fungi, algae).

Total mineralisation is obtained (conversion into CO₂, H₂O, inorganic compounds and biomass under aerobic conditions).

The mineralisation rate is high and is compatible with the composting process.

Those materials that have a degree of biodegradation equivalent to that of cellulose (maximum permissible tolerance 5%) are considered to meet the compostability criteria.

According to ASTM D-5338, for biodegradable plastic materials to be acceptable in composting plants, both biodegradability and disintegration are important. Disintegration is the physical falling apart of the biodegradable plastic material, or more precisely of the product that has been made from it, into fine visually indistinguishable fragments at the end of a typical composting cycle.

Table 3.3: Biodegradability standards requirements (Nolan-ITU, 2002)

Standard	Biodegradation	Requirements
DIN V 54 900	60 wt%	6 months
ASTM D 5338	60 wt%	6 months
CEN 13432	90 wt%	6 months
OECD 207	60 wt%(chemicals)	28 days

The test method used in this evaluation was ASTM D-160: *Standard Practice for Evaluating Microbial Susceptibility of Non-metallic Materials by Laboratory Soil Burial*. This method was chosen over the rest owing to the simplicity of the apparatus used and because it simulates what happens to a material when buried.

A soil container with a depth of at least 12.7 cm should be used. The external environment should consist of apparatus able to maintain a temperature of $30 \pm 2^{\circ}\text{C}$ and 85 to 95% RH. A Labcon Humidity Cupboard set at 30°C was used.

Test specimens should have the shape and size of tensile test specimens. According to the standard, a minimum of three must be used. The exposure period for soil burial must be a minimum of 60 days.

Microbiological susceptibility may be evaluated through:

1. *Visual observation*. Digital pictures were taken throughout the period of 60 days and more detailed observations were performed with the SEM.
2. *Microbial staining* can be evaluated as follows:
 - None – 0
 - Trace (less than 10% coverage) – 1
 - Light (10 to 30% coverage) – 2
 - Moderate (30 to 60% coverage) – 3
 - Heavy (60% to complete coverage) – 4

3. *Property changes* – Tests for physical and mechanical changes, such as tensile strength, flexibility and weight loss, or other tests may be performed as described in appropriate ASTM or other test methods. Tests must be conducted on both unexposed and exposed specimens for the purpose of comparison in determining the extent of microbial degradation of the test material.

For calculating the change in property for each replicate specimen, one of the following equations can be used:

$$C_{e,i} = X_{e,i} - X_o$$

Where $X_{e,i}$ = the measured property of each exposed specimen

X_o = the mean of the property from initial measurements on unexposed specimens.

The following equation can be used to determine the mean value of a property change:

$$\bar{C} = \frac{1}{n} \sum_{i=1}^n C_{e,i}$$

Where n = number of exposed specimens.

The following equation can be used to determine the standard deviation in a property change (Van Soest *et al.*, 1996c):

$$S_c = \sqrt{\frac{1}{(n-1)} \sum_{i=1}^n (C_i - \bar{C})^2}$$

3.4 PLANNING

3.4.1 Seedling tubes

Details of this part of the study are given in Sita *et al.* (2006) and are summarised here. Blends of TPS and recycled PVB from automotive windscreens were investigated. Mechanically compatible blends are formed at low to intermediate starch content. However, SEM and DMA revealed that all the blend compositions investigated had a phase-separated nature. The tensile properties are negatively affected by ageing in a high-humidity environment and they deteriorate rapidly when the samples are soaked in water. However, synergistic property enhancement was observed for a compound containing 22 wt% TPS. It featured a higher tensile strength, shows better water resistance and is significantly less affected by ageing. The work-to-break in tensile mode was significantly higher. This is attributed to plastic deformation of the lower-modulus matrix polymer near the interface with the stiffer starch-rich domains.

TPS with high amylose content yielded the best tensile properties during ageing and was least prone to shrinkage and cracks, which was why it was chosen for further work. Table A1 from Appendix A provides information on the sample compositions chosen for evaluation in this study based on Sita's (2007) results.

The three different compositions incorporating TPS Hi-Maize are given in Appendix A, Table A1. They were called TPS Eu, TPS EMS and TPS PVB. Hi-Maize and Stygel blends, containing 15 wt% glycerol, were prepared and blended with Euremelt 2138 (a polyamide derived from renewable resources) and EMS polyamide. The use of recycled PVB as TPS blend component is advantageous as it reduces the cost of the blend, which is a major stumbling block in the use of biodegradable materials as the polyamides. PVB further improves the mechanical properties, facilitates the moulding of TPS and also improves the material's water resistance. The compositions studied were:

- TPS Eu: 80 wt%TPS (15 wt% G) + 20 wt% Euremelt 2138 + 2 wt % urea
- TPS EMS: 80 wt%TPS (15 wt% G) + 20 wt% EMS + 2 wt% urea
- TPS PVB: 78 wt% TPS (30 wt% G) + 22 wt% PVB + 3 wt% EVA + 2 wt% urea

TPS 15 wt% glycerol and 30 wt% glycerol were also studied.

- TPS 15G containing 15 wt% glycerol was prepared with 15 wt% water, 3 wt% silica, 1 wt% stearic alcohol and 66 wt% Hi-Maize.
- TPS 30G containing 30 wt% glycerol was prepared with 5 wt% water, 3 wt% silica, 1 wt% stearic alcohol and 61 wt% Hi-Maize.

An effort was made to incorporate urea as plasticiser in the compositions, with the purpose of aiding the biodegradation process. It was found that urea is not a very good plasticiser since there was a tendency for these compositions to block the extruder, which was followed by gas evolution and spitting of the material through the die. Thermal degradation was occurring, which was probably the reason for the gas build-up. Even when the temperature was reduced and a smooth extrudate obtained, the injection-moulded test specimens were brown in colour and smelled burnt.

3.4.2 Golf tees

Looking for brittleness in the compositions, it was first attempted to use starch with a high amylopectin fraction, called Stygel. It was expected that the higher amylopectin content would increase T_g , thus lowering the flexibility of the material. The attempt to use a blend of Euremelt 2138 and Stygel starch is illustrated in Figure 3.6. Different ratios of Euremelt 2138 to Stygel were investigated, namely 25:75, 50:50 and 75:25. The Euremelt 2138 was added at different percentages (from 5, 7 up to 10 wt%) to the blends. Addition of more than 10 wt% was judged uneconomical for this application. The ageing of the specimens revealed crack formation caused by the retrogradation of the amylopectin. Unfortunately, even modest addition levels of Stygel to Euremelt 2138 (25:75) resulted in products that showed severe retrogradation. It was decided not to pursue studies on the properties of Stygel blends any further.

Promising results were achieved with blends based on TPS Hi-Maize starch and biodegradable polyester. Polybutylene succinate-adipate (PBSA) with the trade name of Sky Green Polyester SG 200 (Film Grade/FG) (SGPE) was used for the golf tees

applications. The two compositions contained the following ingredients (Appendix A, Table A1):

- 50 wt% SGPE(FG) + 20 wt% urea +20 wt% Hi-Maize starch + 10 wt% stearic acid. For simplicity this composition is named U20/Hi20. (Table A1, sample 1 and 2)
- 50 wt% SGPE(FG) + 40 wt%urea + 10 wt%stearic acid. For simplicity this composition is named U40. (Table A1 sample 3 and 4)

For the compostability tests each of the above mentioned samples were injection moulded in dumb bell and golf tee shapes.

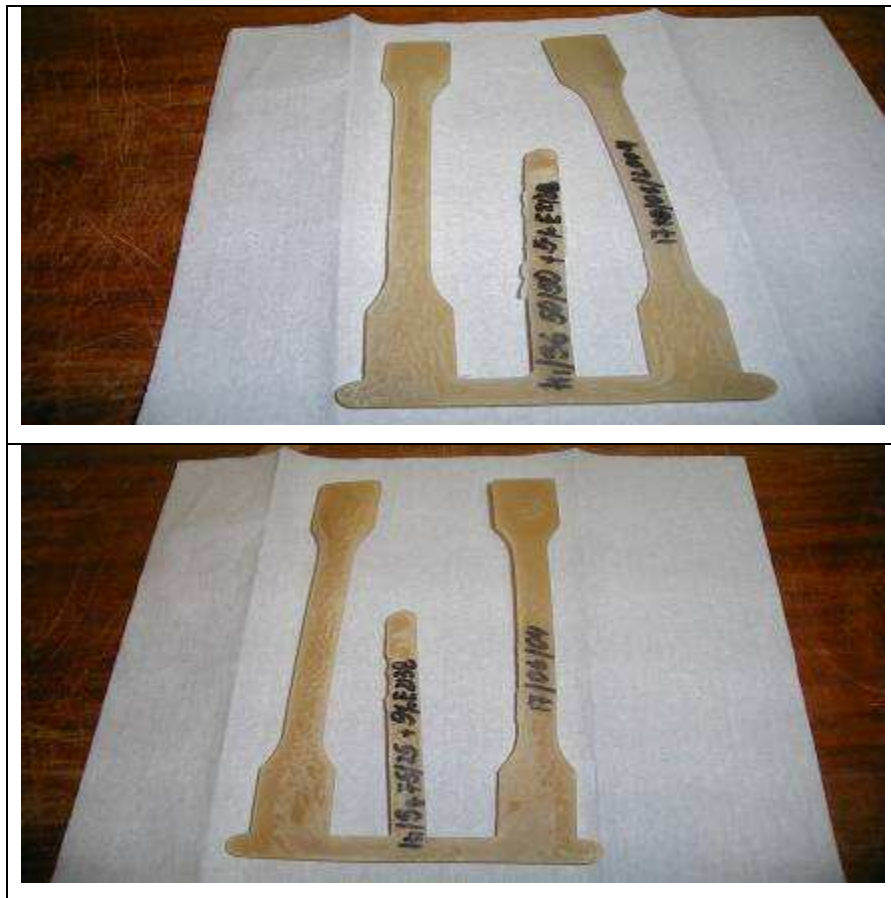


Figure 3.6: Cracked tensile specimens, incorporating Stygel and Euremelt 2138 in different proportions

4 RESULTS AND DISCUSSION

4.1 TENSILE TESTING

The results of the extrusion, injection moulding and tensile testing are given in Appendices A, B and C.

4.1.1 Seedling tubes compositions

All compositions were aged and tested at 60% RH, 30°C and 0% RH, 25°C.

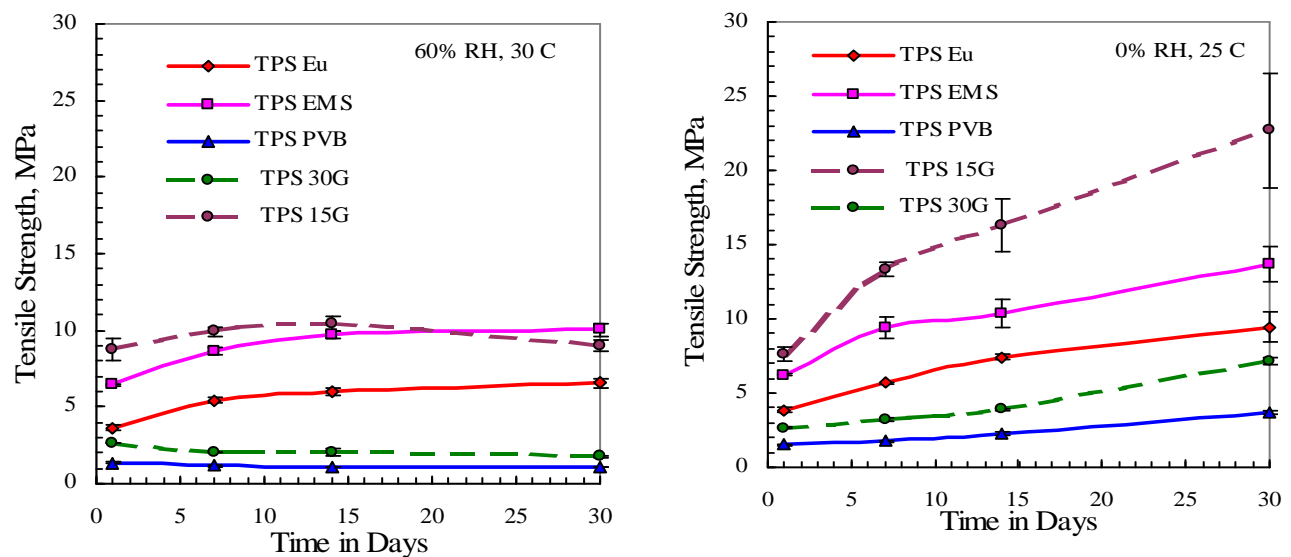


Figure 4.1: Tensile strength of seedling tubes compositions at 60% RH and 0% RH

TPS Eu and TPS EMS showed a very slight increase in tensile strength at 60% RH, 30°C, while the rest of the samples (TPS 15G, TPS 30G and TPS PVB) showed nearly constant strength for the period of 30 days (Figure 4.1). This concurs with the findings of Van Soest and co-workers (1996a,b,c) for materials made from potato starch and aged at 60% RH. They found that there was only a slight increase in B-type crystallinity, leading to a slight increase in the tensile stress and E-modulus, while the elongation at break decreases (Figures 4.2, 4.3 and 4.4).

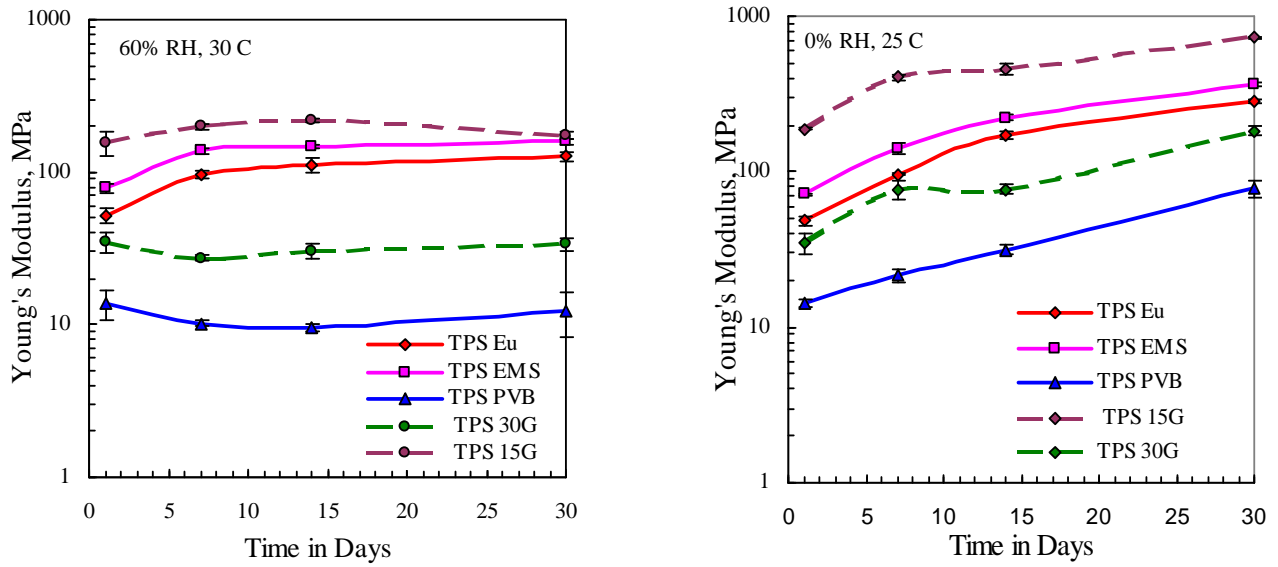


Figure 4.2: Young's modulus seedling tubes compositions at 60% RH and 0% RH

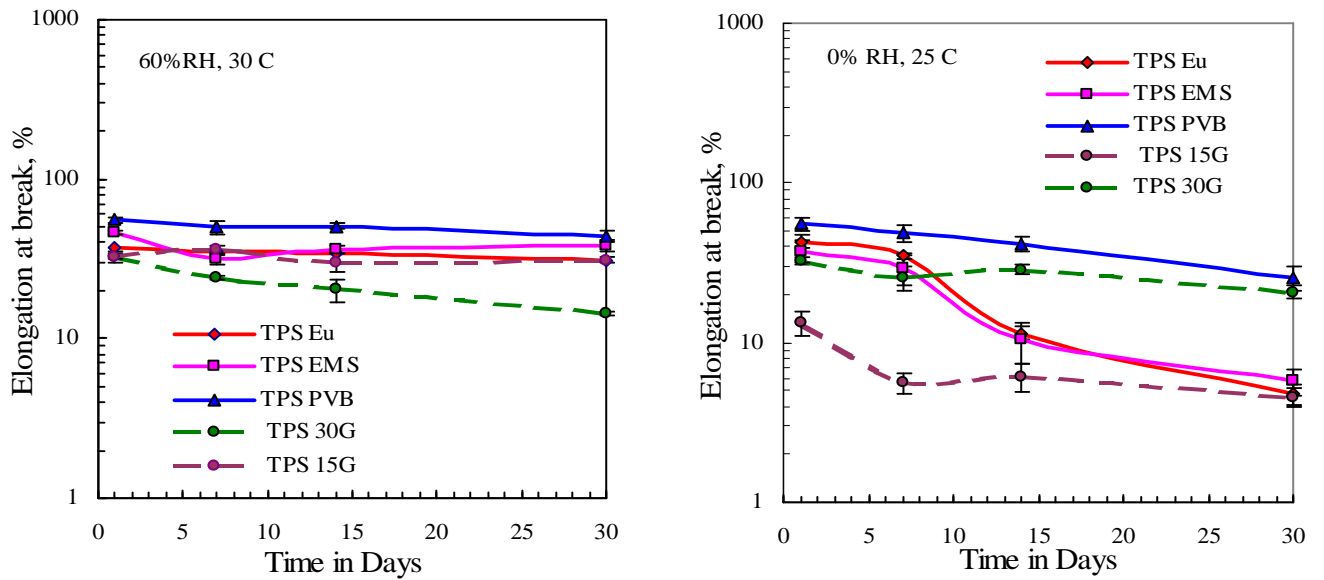


Figure 4.3: Elongation at break for seedling tube compositions at 60% and 0% RH

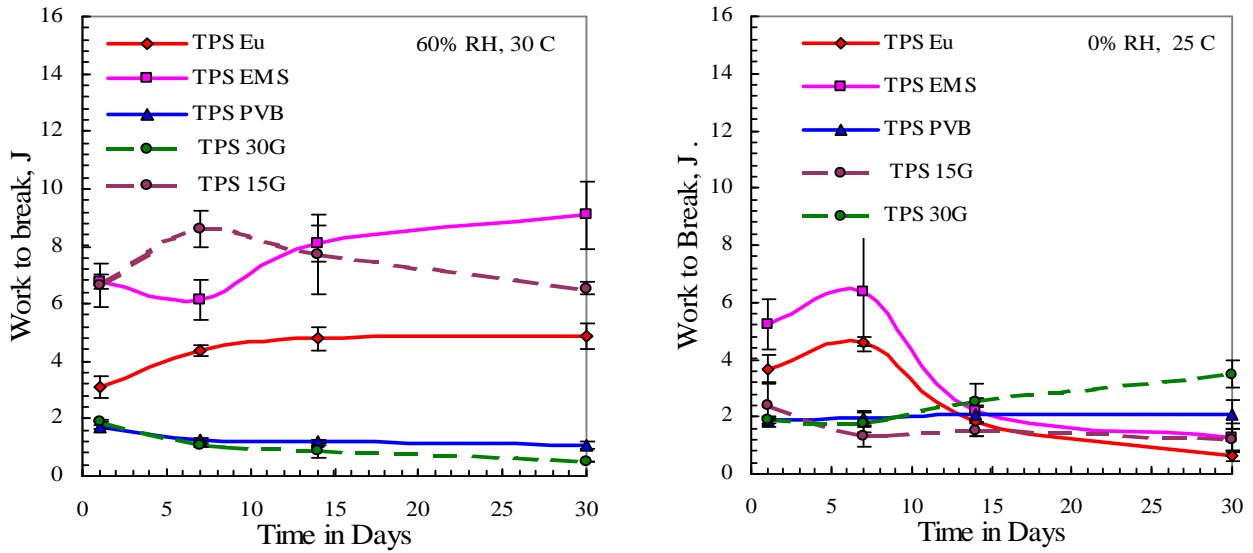


Figure 4.4: Work-to-break for seedling tube compositions at 60% and 0% RH

An increase in the moisture content at the end of the 30 days was noted for the TPS 15G and TPS 30G. The rest of the compositions lost moisture over the ageing period (Figure 4.5 and Table 4.1).

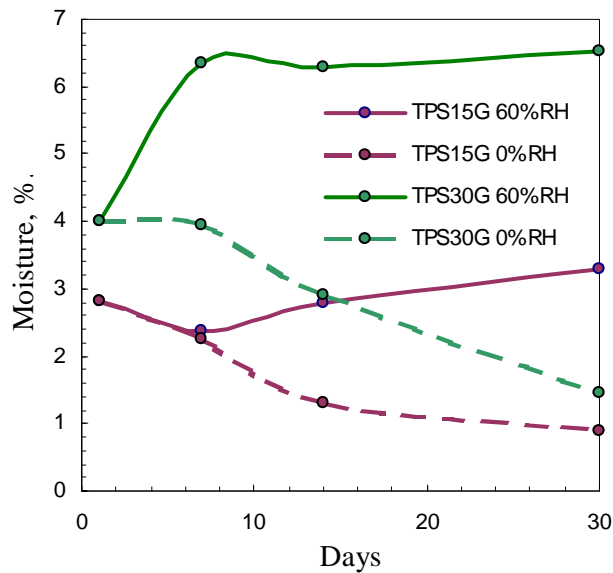


Figure 4.5: Moisture content in TPS 15G and TPS 30G at 60% RH, 30°C and 0% RH, 25°C

Although all samples increased in tensile strength within these 30 days, when aged at 0% RH, the tensile strength of the TPS 15G increased by nearly three times – from 9 MPa to 23 MPa. The samples containing EMS revealed better tensile strength than the ones made from Euremelt 2138, but both blends had lower strength than the TPS 15G.

A decrease in the moisture content was observed for all samples aged at 0% RH. This could be linked to the much higher increase of the tensile strength under these conditions in comparison with the ageing at 60% RH, 30°C (Figure 4.5 and Table 4.1).

The Young's modulus followed a similar pattern to the tensile strength behaviour. It increased when the ageing conditions were changed from 60% RH, 30°C to 0% RH, 25°C.

The elongation at break is very slightly reduced within the ageing period, at 60% RH, 30°C. This slight reduction was observed by Van Soest and co-workers as well (1996 a,b,c) and is explained by the very low amount of B-crystallinity forming under these conditions.

The reduction of elongation at break is more prominent at 0% RH. This could be due to the fact that water, acting as a plasticiser, is lost under the drying conditions. This is very common behaviour for TPS and we can see it here in TPS 15G and the two compositions made from it. At the end of the 30-day period, TPS Eu and TPS EMS showed elongations at break almost equal to that of the TPS 15G.

The characteristic reduction in the elongation between day 5 and day 10 for TPS 15G and TPS 30G is probably connected with the reorganisation of the molecular structures and moisture loss, while after day 15 an equilibrium is reached.

Table 4.1: Moisture content during ageing of seedling tubes and golf tees

Samples/ Moisture, wt%	Day 1	Day 7	Day 14	Day 30	Comment
60% RH, 30°C					
TPS Eu	3.77	-	-	2.30	↓
TPS EMS	3.44	-	-	2.19	↓
TPS PVB	5.32	-	-	4.04	↓
TPS 15G	2.81	2.38	2.79	3.28	↑ (x1.2)
TPS 30G	4.01	6.34	6.30	6.53	↑ (x1.6)
U20/Hi20	1.38	1.15	1.36	1.17	↓
0% RH					
TPS Eu	3.77	-	-	0.61	↓ (x6.2)
TPS EMS	3.44	-	-	1.0	↓ (x3.4)
TPS PVB	5.32	-	-	1.05	↓ (x5.1)
TPS 15G	2.81	2.25	1.30	0.90	↓ (x3.1)
TPS 30G	4.01	3.95	2.90	1.46	↓ (x2.7)
U20/Hi20	1.48	1.12	0.98	0.69	↓ (x2.1)

*An arrow down ↓ shows a decrease and an arrow up ↑ an increase in moisture content

The behaviour of TPS 30G at 0% RH is interesting. It showed much higher moisture losses (Figure 4.5) than TPS 15G. It has higher plasticiser content and shows lower tensile stress but higher elongation at break compared to TPS 15G.

At 60% RH, 30°C, more work to break was needed for the TPS Eu, TPS EMS at the end of the 30 days ageing than at the beginning. For the TPS PVB and TPS 30G the work to break at the beginning and the end of the tests stayed low and was reduced almost by half.

At 0% RH, 25°C there was an increase in the work to break for TPS PVB as well TPS 30G, while a significant reduction of this parameter was observed for the TPS Eu and TPS EMS, which went through a maximum at day 7.

The moisture content of the three samples – TPS Eu, EMS and PVB – reduced with ageing, but this reduction was more rapid when the ageing was performed at 0% RH. The moisture loss for TPS Eu was six times less the initial moisture content at the beginning of the ageing, for TPS EMS it was three times less and for TPS PVB it was five times less.

However, the TPS 15G and TPS 30G showed different behaviours when aged under the two different environments. At 60% RH, 30°C, the samples gained moisture, but when aged at 0% RH, they revealed losses of three times less than the initial moisture content.

4.1.2 Golf tee compositions

Only specimens containing Hi-Maize filler were aged and investigated for change of the tensile characteristics under the two different ageing conditions since the presence of starch could have an influence on their tensile strength. They exhibited an increase in their tensile strength and elastic modulus with ageing, although they had higher elongations at break and required more work to be broken (Figure 4.6).

The specimens having only urea as filler showed no changes in the crystallinity on the XRD spectrum over a period of 30 days (Spectrum 9). Their tensile values are shown on the graphs (Figure 4.6) with a red dot. They had lower tensile strength and a lower Young's modulus than those with both urea and starch filler, less elongation at break and needed less work to break.

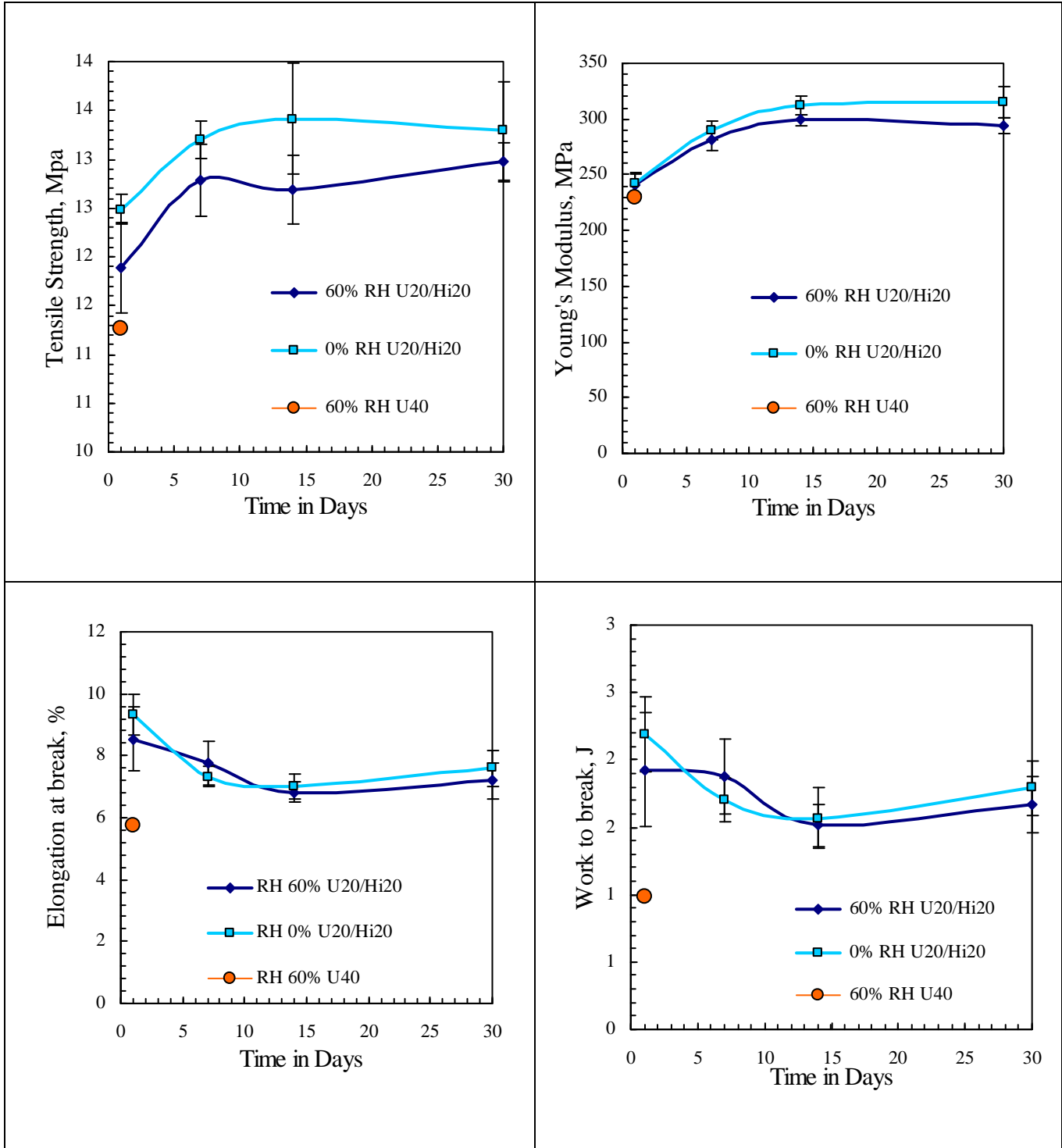


Figure 4.6: Tensile properties of golf tees compositions at 60% and 0% RH

For the starch blends with Hi-Maize as filler it was interesting to see the influence of moisture content on the tensile properties (Figure 4.7). Up to day 7 both samples aged under different conditions had reduced moisture content. For the samples studied under 0% RH, the moisture content continued to reduce after day 7, whereas for those aged at 60% RH an increase in the moisture was initially observed, and then a steady reduction after day 15.

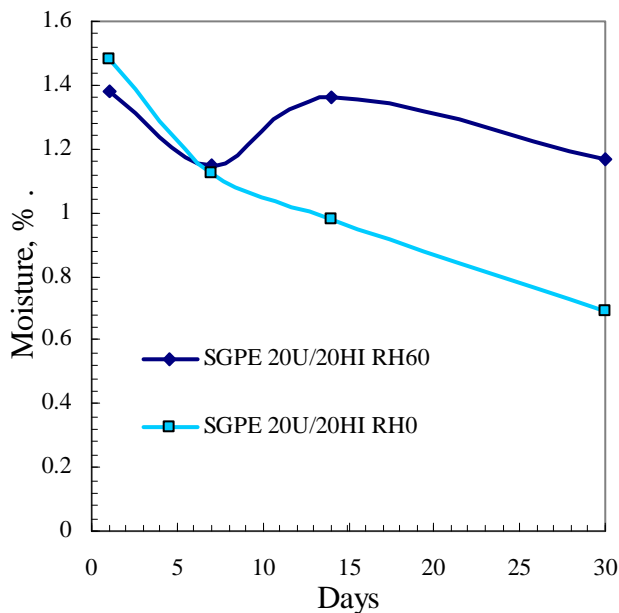


Figure 4.7: Moisture change in starch-filled golf tees compositions over 30 days

4.2 XRD RESULTS

4.2.1 Seedling tubes compositions

There are a total of 11 spectra, all displayed in Appendix D – XRD data.

The diffractograms were used to study the changes in the material in a more qualitative way, according to the sharpness and the size of the crystallinity peaks. Quantitative determination of the crystallinity was not the aim of this study.

Spectrum D1 is a spectrum of Virgin Hi-maize starch from 5-70 2θ . Starch is a semi-crystalline polymer and it has three crystalline peaks, which appear around $2\theta=17-22^\circ$.

Spectrum D2 shows the spectra for TPS Eu and each of the raw materials incorporated into this composition. TPS Eu is much more crystalline than the amorphous Euremelt 2138, which has a broad amorphous peak at $2\theta=19.5^\circ$. Three sharp peaks appear at $2\theta=19.5^\circ$, $2\theta=12.5^\circ$ and $2\theta=22.5^\circ$.

Spectrum D3 shows the spectra for TPS EMS and each of the raw materials incorporated into the composition. TPS EMS has more crystallinity or sharper peaks compared with the amorphous EMS. The three crystalline peaks observed for TPS Eu appear here as well.

Spectrum D4 shows the spectra for TPS PVB and each of the raw materials incorporated into the composition. As with TPS Eu and TPS EMS, the spectrum of the third sample of TPS PVB has very much the same peaks.

In Spectra D2, D3 and D4, the raw materials show different amounts of crystallinity of the polymers involved in the blends. The highest crystallinity is observed for TPS EMS, with a peak at $\theta=21^\circ$, while TPS PVB and Euremelt display wide amorphous peaks at $\theta=19.5^\circ$.

The spectra for TPS 15G and TPS 30G show some broad crystalline peaks at $2\theta=12.5^\circ$ and $2\theta=19.5^\circ$.

Spectrum D5 shows the spectra for TPS Eu, EMS and PVB, as well TPS 15G and TPS 30G, aged at 60% RH, 30°C. The samples were aged for a period of 30 days at 60% RH, 30°C to check if there would be changes.

Spectrum D6 shows the spectra for TPS Eu, EMS and PVB aged at 0% RH. Characteristic shifts in the spectra of TPS 30G and TPS PVB, which are made from TPS 30G, were observed when the ageing was done at 0% RH. Spectrum D7 combines Spectrum D5, when the samples were aged at 60% RH, and Spectrum D6, when the samples were aged at 0% RH.

The three blends – TPS Eu, EMS and PVB – have similar crystallinity characteristics (spectra), which do not change significantly with a change in the ageing conditions from dry to humid. A shift in the spectra of TPS 30G and the blend with PVB, when aged at 0% RH, is observed. Virgin EMS appears to be more crystalline than virgin PVB and Euremelt 2138. This is why the blend of Hi-Maize with Virgin EMS shows more crystalline behaviour.

4.2.2 Golf tee compositions

Spectrum D8 shows the spectrum for U40. The 40 wt% urea used as filler forms a complex with SGPE, having two groups of crystalline peaks at $2\theta=19.5^\circ/20.5^\circ/21.5^\circ/22.5^\circ$ and $2\theta=25^\circ/26.5^\circ/27.5^\circ$.

Spectrum D9 shows the ageing of the specimens containing 20 wt% urea and 20 wt% Hi-Maize over 30 days. No changes were observed during the ageing at days 1, 7, 14 and 30. At $2\theta=19.5^\circ/21.5^\circ/22.5^\circ$, the peak at $2\theta=20.5^\circ$ is much smaller. The peaks in the second group appear to be much smaller in size at $2\theta=25^\circ/26.5^\circ/27.5^\circ$, which is an indication that the crystallinity has been reduced by the addition of starch.

Spectrum D10 combines Spectrum D8 of U40 and Spectrum D9 of U20/Hi20. Overlapping the two spectra clearly shows the difference in the crystallinity, with greater crystallinity being achieved when only urea was used as filler.

Spectrum D11 gives an indication of the raw materials involved in the composition U20/Hi20.

4.3 COMPOSTABILITY

4.3.1 Seedling tubes compositions

The results of the compostability tests and the viability control are presented in Appendix E. The compostability was studied according to the test method ASTM G160. An inoculum was collected from Weltevreden composting municipal grounds at Brakpan. The mixture was aged for three months, as well as resifted on a regular basis through a mesh screen. The viability control for the tensile strength of untreated cotton cloth of 400 to 475 g/m² had a loss of 55 wt% strength, which complied with the standard requirement.

The pH of the soil was tested at the beginning and at the end of the test and showed no significant changes over the testing period. One part by weight of soil was mixed with 20 parts by weight of water. The mixture was shaken, allowed to settle and after one hour, the reading was taken.

The moisture content was kept between 20 and 30 wt% and measured at 105°C with a moisture analyser. Table 11 in Appendix E shows the changes in the moisture content of the soil. The two soil containers were made of HDPE. To be able to keep the temperature at 30 ± 2 °C, a Labcon humidity chamber was used. It was supplied with a saturated solution of K₂SO₄, acting as a humidity stabilise (RH calibration with saturated salts (s.a.10) <http://www.natmus.dk/cons/tp/satsit/satsalt.htm>, [2007, January 29];

Equilibrium Relative Humidity (s.a.11)

<http://www.omega.com/temperature/Z/pdf/z103.pdf>, [2007, January 29]).

From three to five standard tensile test specimens were buried in the soil. The properties of the samples were studied for 60 days at days 0, 7, 14, 30, 45 and 60. Care was taken when removing the test specimens not to disturb the soil bed, which could affect the growth of soil microbes and cause inconsistent results.

The visual observations at the beginning and the end of the exposure period are reflected in Figure 4.8 below.

Day 0



Day 60



Figure 4.8: Visual observations of seedling tubes compositions at day 0 and day 60 of the composting

Parallel to the ASTM G160 test method, PVB composting behaviour was studied by means of burial in a greenhouse (Figure 4.9).



Figure 4.9: Observation of the plant roots growing through a PVB tube placed in the greenhouse

At the beginning of the study TPS was produced from both Hi-Maize and Stygel starches. The tubes made from the latter started to fall apart during the first few weeks in the greenhouse. A decision was then taken not to pursue the use of any Stygel further. Numerous other experiments were also conducted with additional processing aids to try and enhance the melt flow properties of the TPS-PVB mixtures during injection moulding and thereby to eradicate the weld line problem. Satisfactory results for eliminating the weld line during injection moulding and having the roots of the plant growing through the tube were achieved using a 3 mm wall thickness.

The microbial staining of all samples is evaluated in Table 4.2.

Table 4.2: Estimation of microbial staining for all samples (ASTM G160)

Observed growth or stain	Rating*	Material	Observation/Comment
None	0		
Trace (less than 10% coverage)	1	U20/Hi20	Yellow/brownish staining
Light (10 to 30% coverage)	2	U40	Yellow/brownish staining
Moderate (30 to 60% coverage)	3		Black growth
Heavy (60 % to complete coverage)	4	TPS Eu/ EMS/PVB	Heavy black growth

* Rating according to ASTM G160

Property changes such as tensile strength, flexibility and weight loss are shown in Table 4.3 and Figure 4.10. The seedling tubes and golf tees samples have close to 100% reduction in tensile strength and Young's modulus, which is satisfactory.

Table 4.3: Changes in tensile strength

Tensile strength (MPa)	Day 0	Day 60	Difference	Change in property (%)	Standard Deviation
TPS Eu	6.5	0.0004	-6.5	-100	0
TPS EMS	10.4	0.0011	-10.4	-100	0
TPS PVB	1.3	0.0017	-1.3	-100	0
U20/Hi20	12.4	0.0040	-12.4	-100	0
U40	11.2	0.0021	-11.2	-100	0

Note: The negative sign in front of the change in the properties indicates reduction in the property at the end of the testing period. The positive sign indicates an increase in the property at the end of the testing period.

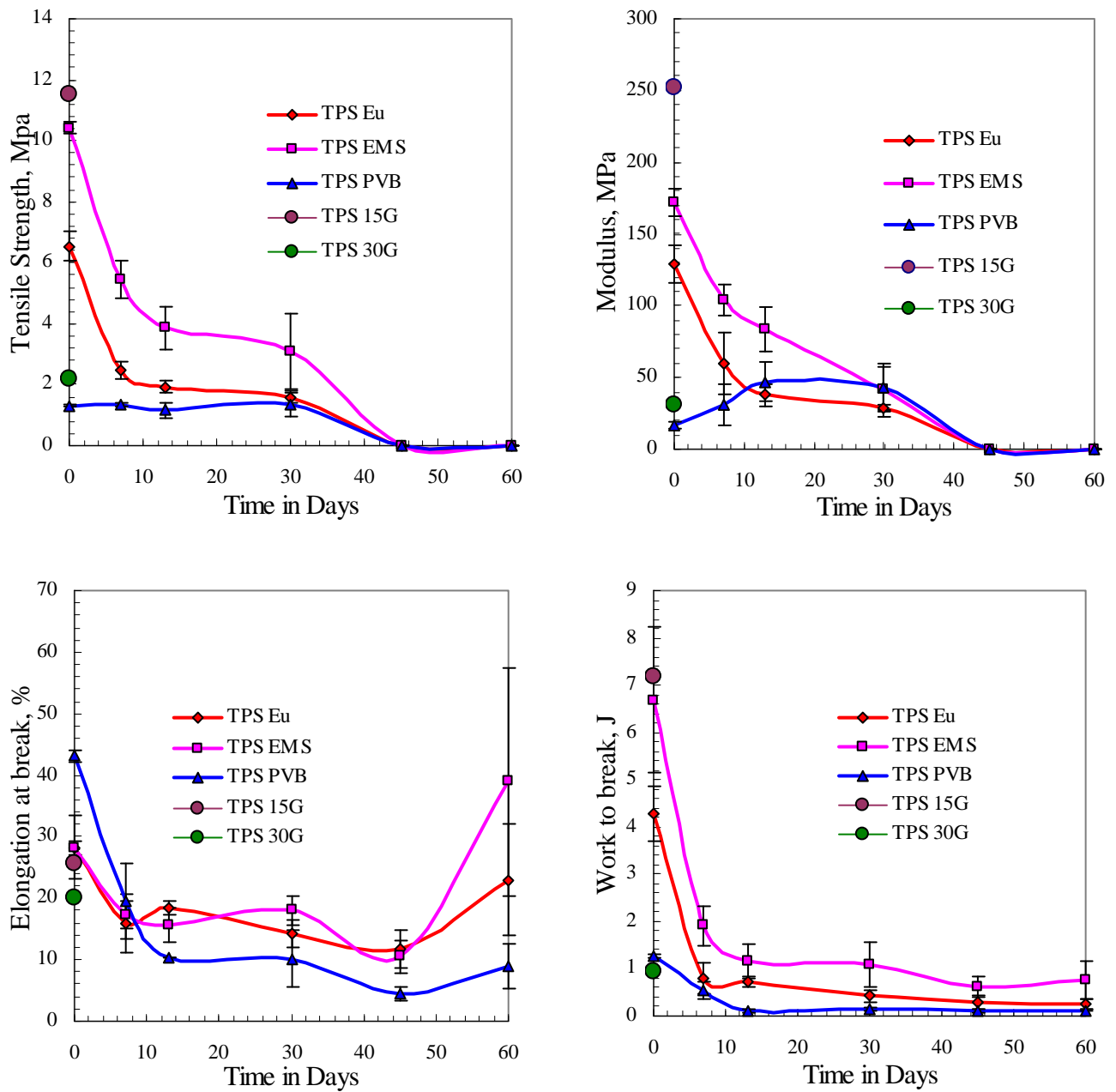


Figure 4.10: Tensile properties of seedling tubes compositions under controlled composting conditions

It must be mentioned that samples of TPS 15G and TPS 30G were not able to undergo tensile testing after day 7 since they had disintegrated into pieces and could be regarded as biodegradable straight away.

Table 4.4: Changes in elongation at break

Elongation at break (%)	Day 0	Day 60	Difference	Change in property (%)	Standard Deviation
TPS Eu	28.2	22.9	-5.3	-18.4	9.0
TPS EMS	28.3	39.0	10.7	37.9	18.5
TPS PVB	43.1	8.9	-34.2	-79.3	3.0
U20/Hi20	6.8	6.7	-0.1	0.1	0.9
U40	5.8	3.8	-2.0	34.2	0.9

It is interesting to note the change in the elongation at break (Table 4.4). For the seedling tubes there is a reduction in the initial property for TPS Eu and TPS PVB. Such a reduction was expected for TPS EMS as well since the XRD crystallinity of the three samples is comparable. Contrary to expectations, however, there was an increase in the elongation at break from 28% to 39%. Unfortunately, this composition has to be disregarded for future use and biodegradability tests for seedling tubes compositions since such toughening in the material does not bring about fast biodegradation.

The reductions in the elongation at break for TPS Eu and TPS PVB were respectively 18% and 79%. TPS PVB, which had the highest reduction in the elongation at break, qualifies as the 'winning' composition among all three compositions tested for seedling tubes, although a residual elongation of 8% was still recorded on the final day of testing. This was regarded as satisfactory since the customer had requested that the tubes should have some strength, enough to keep them intact up to three months after they had been planted in the soil.

The optical microscopic photos of TPS EMS show much more homogeneous blending between TPS 15G and EMS than with PVB or Euremelt 2138 (Figure 4.11).

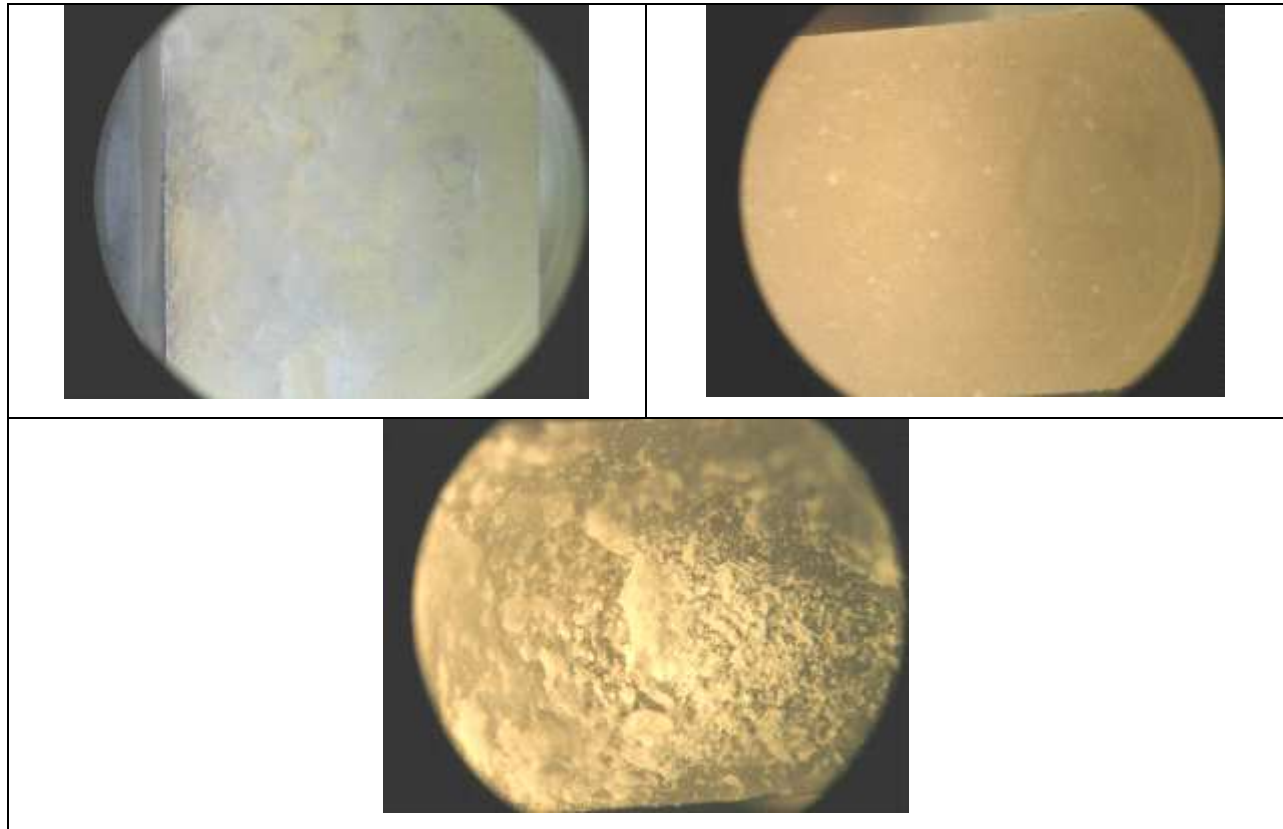


Figure 4.11: Optical microscopy results of TPS Eu (top left), TPS EMS (top right) and TPS PVB (bottom) at a magnification of x40

The results from the optical microscopy revealed homogeneity in the blends of TPS EMS and phase separation for TPS Eu and TPS PVB. Such homogeneity for TPS PVB has been confirmed by DMTA by Sita *et al.* (2006). It is concluded that at low TPS loadings, starch-rich domains act as physical reinforcements for the PVB matrix. The loss in mechanical properties above the 50 wt% TPS content is ascribed to the starch phase becoming the continuous phase (Sita *et al.*, 2006).

4.3.2 Golf tees compositions

4.3.2.1 Visual observation, at the end of the exposure period

Figures 4.12 and 4.13 show visually the state of the golf tees at the beginning and end of the exposure period, and Figure 4.14 shows the tensile strength properties of the golf tees compositions under controlled composting conditions

Day 0



Day 60



Figure 4.12: Visual observation of golf tees compositions U20/Hi20 at day 0 and day 60 of the composting

Day 0



Day 60



Figure 4.13: Visual observation of golf tees compositions U40 at day 0 and day 60 of the composting

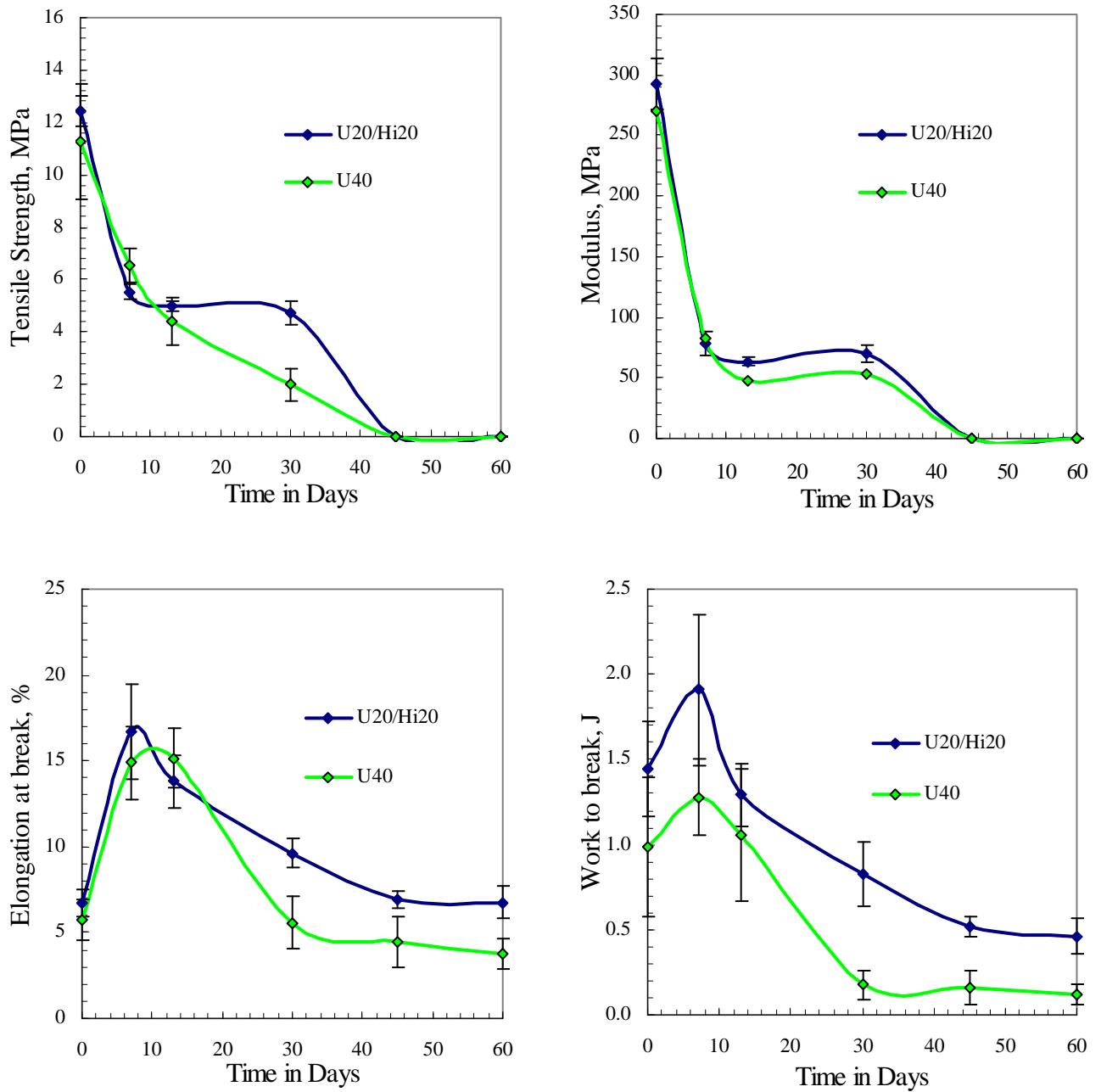


Figure 4.14: Tensile properties of golf tees compositions under controlled composting conditions

To test the golf tees' compostability, the tensile property changes were combined with the weight loss study. In contrast to the starch compositions, which incorporated around 80 wt% of Hi-Maize, the golf tees had only 20 wt% Hi-Maize, which made the weight loss test easy. When weight percent of Hi-Maize was predominant in the composition, difficulties obtaining weight loss results were experienced.

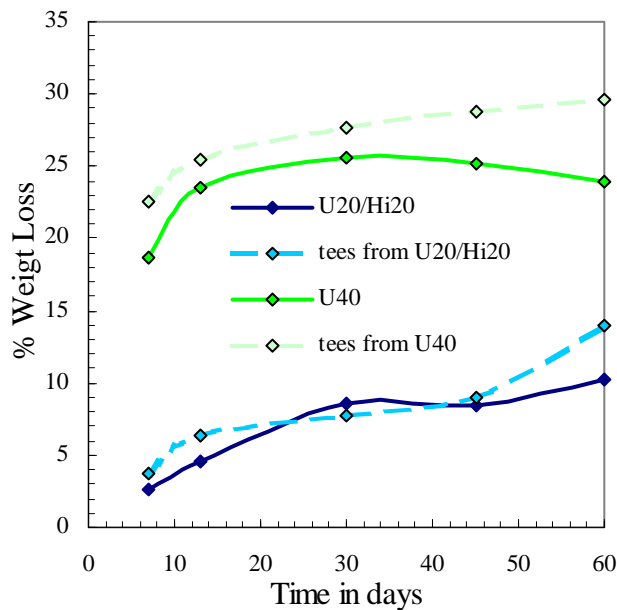


Figure 4.15: Weight loss of golf tees compositions under controlled composting conditions

The graph of the weight loss of the golf tees compositions (Figure 4.15) indicates that weight loss occurred according to the size of the specimen; the smaller the specimen, the bigger the weight loss during the composting period. Tees of the two different compositions lost more weight than the very same specimens made into dumb-bell shapes for tensile strength testing, which are much larger in size.

The composition containing only urea as filler had the greater weight loss of the two. The fact that of the two compositions, the one containing only urea has a higher percentage of biodegradability was proved from studying the results of the SEM and XRD analyses.

4.4 SEM RESULTS

The scanning electron microscopy (SEM) photos are contained in Appendix F – SEM data.

Example of SEM abbreviations:

1_7in1(x1000)

1 indicates the date of the compostability test (days 1, 7, 13, 45, 60, etc.)

7 indicates the number of the sample, in this case E 2138

'In' or 'out' indicates whether the photo was taken in (the inner part of the sample) or out (the outer part) of the cut for SEM specimen.

1 - the number in front of the magnification brackets is the number of pictures taken at this magnification and aging conditions. In this case only one picture has been taken.

The number in brackets is the magnification.

All samples were studied for a period of 60 days, parallel to the biodegradation process taking place.

The microorganisms' activity was clearly observable in the TPS 15 and TPS 30 samples. Hife (a type of microorganism) with collapsed cell walls was noted in two photos of TPS 15, 45_5in1 (x1000) and 45_5in4(x3700) (Appendix F, Figures F1 and F2). Together with it some type of crystalline structure (bottom right) was observed. These could be crystals of vitamins, produced from the microorganisms, or from the soil or sand structures.

In TPS 30G extra-cellular slimy mucus, produced by the bacteria, is seen in the outside layer of the cut sample in 13_6out1(x3700) (Appendix F, Figure F3).

Spores of hife in TPS Eu were observed in photo 13_7out1(x7000) (Appendix F, Figure F4).

So-called pitting (Appendix F, Figure F6), or the start of the degradation process, which is caused by enzymatic activity, is observed in the TPS EMS photo 13_8in3(x7 000) as well as a broken starch granule in photo 7_8in2(x500) (Appendix F, Figure F5).

The slimy effect of the bacterial activity in TPS PVB can be seen in photo 7_9in2(x3700) (Appendix F, Figure F7). Even with the naked eye the author was able to see two distinct layers of biodegradation when the sample was cut. It is clear that two different types of microorganism were creating (1) the outside layer (aerobic) and (2) the inside layer (anaerobic) 45_9out1(x20) (Appendix F, Figure F8). Hife activity is noticed here again in 45_9out2(x3700) (Appendix F, Figure F9)

In the golf tees compositions containing Hi-Maize and urea, the activity of the enzymes and microorganisms is clearly visible, but starch granules were still found at day 60; these can be spotted in the anaerobic inside layer in 60_1in3(x3700) (Appendix F, Figure F10). In the aerobic layer there appears to be full decomposition in 60_1out3(x1400) (Appendix F, Figure F11)

Complete degradation is observed on the inner and outer sides of the cut samples having urea as filler, shown in 60_3in 4(x3 700) (Appendix F, Figure F12). This degradation is more complete than in the samples with the starch-filled compositions.

5 CONCLUSIONS

Attempts were made to prepare starch-based plastic compounds for biodegradable, injection-moulded seedling tubes and golf tees. Sappi Forest Products SA needed partially biodegradable tubes to be able to increase the productivity of their seedlings. Biodegradability, brittleness and low cost are what the golf tee market is currently looking for.

For the seedling tube compositions, blends of thermoplastic starch (TPS) and polymers were prepared via extrusion, followed by injection moulding. Two types of polyamides were used: low-molecular-weight Euremelt 2138 and copolymer EMS Grilon BM13 SBG, as well recycled polyvinylbutyral (PVB). They all formed compatible, rather than miscible, blends with TPS.

For the golf tee compositions, synthetic polyester polybutylene succinate adipate (PBSA) was incorporated as the main ingredient in the blends. Adding fillers such as urea and starch reduced the cost of these blends. Same process methods of extrusion and injection moulding apply for the golf tee compositions.

Characterisation of the blends was achieved through mechanical testing, X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), optical microscopy and ASTM G160 biodegradability burial testing.

A number of conclusions can be drawn from the analysis of the experimental results.

5.1 SEEDLING TUBES

The availability of a continuous supply of Hi-Maize is uncertain. Blends with Stygel were therefore considered. However, the experiments with Stygel resulted in compounds that suffered severe retrogradation. Acceptable mechanical properties were achieved only when high-amylose starch, e.g. Hi-Maize, was incorporated into the blends.

A change in the ageing conditions from 60% RH to 0% RH had an enormous effect on the mechanical tensile strength properties of the compositions. At 60% RH, 30°C, the blends used for the seedling tubes had lower tensile strength and a lower elastic modulus, but higher elongation at break in comparison with the TPS 15G and TPS 30G. No significant changes were observed due to the fact that very little B-crystallinity is present under these drying conditions. The moisture gain in TPS 15G and TPS 30G under these conditions brought about higher strength in the TPS than in the blends. Under drying conditions the low B-crystallinity is predominant in determining the mechanical characteristics of the blends. The moisture gain influences the material slightly.

The trend in the changes in tensile strength properties was the same when the ageing was performed at 0% RH. Moisture losses, however, were four to six times greater than at the beginning of the experiment. Much higher increases in the tensile strength and elastic modulus, and greater decreases in the elongation at break were observed for the compositions aged at 0% RH than for those aged at 60% RH.

The glycerol has a greater plasticising effect on the compositions than water. Compositions with 15 wt% glycerol and 15 wt% water had higher tensile strengths and elastic moduli and less elongation at break than those with 30 wt% glycerol and 3 wt% water.

The blends TPS Eu and TPS EMS showed a similar pattern of crystallinity, which was not influenced by the change in the ageing conditions from humid to dry. Virgin EMS appears to be more crystalline than PVB and Euremelt 2138, which is why the blend with Hi-Maize showed more crystalline behaviour. TPS EMS could not be considered for seedling tubes compositions because, although it has highest tensile strength and the best compatibility of the ingredients, according to the optical microscopy results it has the worst susceptibility to biodegradation. TPS PVB has a shift in the spectrum to the right when aged under dry conditions. The same shift is observed for the TPS 30G under 0% RH.

Complete degradation of TPS 15G and TPS 30G within seven days of composting was noticed. No mechanical testing results on these compositions were available for that reason. Of the polyamide-starch blends, the one with Euremelt 2138 decomposed more easily than the one with EMS Grilon.

An interesting trend in behaviour was observed with the mechanical strength testing of the PVB blends during composting. The elastic modulus and tensile strength increased with ageing, reached a plateau and then dropped again, whereas the mixes with polyamide showed deterioration in these properties with an increase in the composting time, also showing a plateau between day 10 and day 30 of the composting period. On the other hand, TPS PVB had the lowest tensile strength and elastic modulus and an 80% reduction in the elongation at break during the compostability tests. This is the composition finally chosen for the seedling tubes. A shift in the XRD spectra of TPS 30G and the blend TPS PVB was observed, which could explain the different composting behaviour of the blend in comparison with the polyamide blends.

The processing properties of these materials, such as compounding and shaping, are poor compared with those of conventional plastics. The mechanical properties and ageing behaviour of Hi-Maize TPS blends are sensitive to the type of polymer, the amount of plasticiser and the processing additives used, and to the moisture content and amount of water. More research is necessary to solve these problems before commercialisation can be considered.

5.2 GOLF TEES

The mechanical properties of blends containing starch are not affected by changes in the ageing conditions. The compostability tests on the polyester blends containing 20 wt% starch showed unexpected slower decomposition than the blends containing only urea filler. This phenomenon could be explained by the strong interaction between urea and starch, which probably led to cross-linking in the compositions. A weight loss of only 15 wt% for compositions with 20 wt% Hi-Maize and 20 wt% urea was achieved.

Biodegradation of 30 wt% for golf tees compositions containing 40 wt% urea filler was obtained. These results were accompanied by higher crystallinity and lower tensile strength characteristics in U40 compositions.

The size of the test specimen during composting is important. Tees of both different golf tees compositions had greater weight loss than the very same compositions made into a dumb-bell shape.

SK Chemicals Korea has discontinued the production of Skygreen polyester SG200 (FG). Other suppliers of PBSA should be found if commercialisation is required.

6 REFERENCES

African Products (Pty) Ltd (s.a.1) Basic starch chemistry, *Presentation*.

African Products (Pty) Ltd (s.a.2) Starch modification and application, *Presentation*.

ASTM D 5338 (1992) *Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials under Controlled Composting Conditions*.

ASTM G 160 (1998) *Standard Practice for Evaluating Microbial Susceptibility of Nonmetallic Materials By Laboratory Soil Burial*.

ASTM G 160 (s.a.3), <http://www.astm.org>, [2004, March 4].

Bellis, M. Inventors, <http://inventors.about.com/library/inventors/blgolfteehtm.htm> [2004, March 4].

Biodegradable Polyesters: Packaging goes green (s.a.4)
<http://www.plasticstechnology.com/articles/200209fa3.html>, [2004, June 07]

Buhler, F.S., Schmid, E. and Schultze, H.J. (1995), Starch mixture and process for production thereof, US Patent 5436078, assigned to Ems-Inventa AG.

Chapter1 (s.a.5) <http://scholar.lib.vt.edu/theses/available/etd6998-172444/unrestricted/CHAPTER1.PDF> [2004, February 19].

Cheremisinoff, N.P. (1993) *An Introduction to Polymer Rheology and Processing*, CRC Press, London.

Chen, W., David, D.J., Mac Knight, W.J. and Karasz, F.E. (2001) Miscibility and morphology of blends of poly(3-hydroxybutyrate) and poly(vinyl butyral). *Polymer*, Vol. 42, (20), 8407-8414.

Dubois, P. and Narayan, R. (2002) Biodegradable compositions by reactive processing of aliphatic polyester/polysaccharide blends, 7th European symposium on polymer blends, 198(1), 233-244.

Equilibrium Relative Humidity (s.a.11)

<http://www.omega.com/temperature/Z/pdf/z103.pdf>, [2007, January 29]

Forsell, P.M., Mikkila, M., Moates, G.K. and Parker, R. (1997). Phase and glass transition behaviour of concentrated barley starch-glycerol-water mixtures: A model for thermoplastic starch. *Carbohydrate Polymers*, 34, 275 - 282.

Godbole, S., Gote, S. and Chakrabarti, T. (2003) Preparation and characterization of biodegradable poly-3-hydroxybutyrate – starch blend films, *Bioresource Technology*, 86, 33 - 37.

Golding, S. (1998) *The effects of annealing on structural and mechanical properties of starch films*, unpublished.

Graaf, R.A., Karman, A.P. and Janssen L.P.B.M. (2003) Material properties and glass transition temperatures of different thermoplastic starches after extrusion processing, *Starch*, 55, 80 - 86.

Hammer, C.F., Paul, D.R. and Newman, S. (1978) *Polymer Blends*, Vol. 2, Academic Press, New York, USA, pp 217 - 219.

History George F. Grant (s.a.6), <http://www.ourgolf.com/history/georgegrant.htm> [2004, March 4].

Hizukuri, S. (1986), *Carbohydrate Res.*, 147, 342.

Hoseney, R.C. (1994) *Principles of Cereal Science and Technology*, 2d Ed, American Ass. Of Cereal chemists, Inc., St.Paul, Minnesota, USA.

Hoshino, A., Sawada, H., Yokota, M., Tsuji, M., Fukuda, K. and Kimura, M. (2001) , *Soil Science & Plant Nutrition*, 47, 35.

Huang, S.J. and Edelman, P.G. (1995) *An overview of biodegradable polymers and biodegradation of polymers*, in: *Degradable Polymers: Principles and Applications*, Scot, G. and Gielead, D., Eds., Chapman & Hall, Chapter 2, pp 18 - 28.

ISO 846 (1978) *Determination of Behaviour under the Action of Fungi and Bacteria-Evaluation by Visual Examination or Measurement of Change in Mass or Physical Property*.

Jang, J.K. and Pyun, Y.R. (1997) Effects of moisture on crystallinity of wheat starch at different temperatures, *Starch*, 49 (7-8), 272 - 277.

Janik, H., Justrebska, M. and Rutkowska, M. (1998) Biodegradation of polycaprolactone in sea water, *Reactive Functional Polymers*, 38, 27.

Jasberg, B.K. and Shogren, R.L. (1994) Ageing properties of extruded high-amylose starch, *Journal of Environmental Degradation*, 2, 99 - 109.

Jenkins, R., Gould, R.W. and Gedcke, D. (1981) *Quantitative X-Ray Spectrometry*, Marcel Dekker, Inc., pp 1 - 4.

Jiogao, Y., Songzhe, C., Jianping, G., Huawu, Z., Jie, Z. and Tong, L., (1998) A study on the properties of starch/glycerin blend, *Starch*, 50 (6), 246 - 250.

Kalichevsky, M.T., Jaroszkiewicz, E., Abilet, S., Blanshard, J.M.V. and Lillford, P.J. (1992) The glass transition of amylopectin measured by DSC, DMTA and NMR. *Carbohydrate Polymers* 18, 77 - 78.

Kaplan, D.S. (1976) Structure-property relationships in copolymers to composites: Molecular interpretations of the glass transition phenomenon, *Journal of Applied Polymer Science*, 20, 2615 - 2629.

Khalil, M.I., Farag, S., Aly, A.A. and Hebeish, A. (2002) Some studies on starch-urea-acid reaction mechanism, *Carbohydrate Polymers*, 48, 255 - 261.

Kollinsky, F. and Markert, G. (1971) *Multi-component Polymer Systems*, ACS, Washington, D.C., p 175.

Kruger, A. (2003) *Starch-based Plastics for Injection Moulding*, Status Report, CSIR, Pretoria, RSA.

Lim, S.W., Jung, I.K. and Jin, B.S. (1999) Structure and properties of biodegradable gluten/aliphatic polyester blends, *Eur. Polym. J*, 35, 1875 - 1881.

Liu, Z.Q., Yi, X.S. and Feng, Y. (2001) Effects of glycerol monostearate on the performance of thermoplastic starch, *J. Mat. Sci.*, 36, 1809 - 1815.

Meadows, C. (1998) *The Effects of Ageing on Biodegradable Starch Plastic Films*, BEng Thesis, University of Queensland, Australia

Myllarinen, P., Partanen, R., Seppala, J. and Forssell, P. (2002) Effect of glycerol on behaviour of amylose and amylopectin films, *Carbohydrate Polymers*, 50, 355 - 361.

Narayan, R., Barengerg, S.A., Brash, J.L. and Redpath, A.E. (1990) *Introduction, In: Degradable Materials: Perspectives, Issues and Opportunities*, CRC Boston, pp 1 - 37.

Nolan-ITU Pty (Ltd) (2002) *Biodegradable plastics – Development and environmental impacts*, <http://www.deh.gov.au/industry/waste/biodegradable/index.html> [2004, May 17].

Paul, D.R. and Newman, S. (1978) *Polymer Blends*, Vol. 2, Chapter 12, New York, Academic Press, p 35.

Phillips, J. W. (1998) *Mechanical Behaviour of Materials*, TAM 224/CE 210.

Purushothaman, M., Anderson, R.K.I., Narayana, S. and Jayaraman, V.K. (2001) *Bioprocess & Biosystems Engineering*, 24, 131.

Rao, M.A. and Hartel, R.W. (1998) *Phase/State Transitions in Foods*, Marcel Dekker Inc, New York, USA.

Ratto, J.A., Stenhouse, P.J., Auerbach, M., Mitchell, J. and Farrell, R. (1999) Processing, performance and biodegradability of thermoplastic aliphatic polyester/starch system, *Polymer*, 40, 6777 – 6788.

RH calibration with saturated salts (s.a.10)

<http://www.natmus.dk/cons/tp/satsit/satsalt.htm>, [2007, January 29].

Ritchie, P.D. (1972) *Plasticizers, Stabilizers and Fillers*, Glasgow, UK.

Rutkowska, M., Krasowska, K., Heimowska, A., Smiechowska, M. and Janik, H. (2000) The influence of different processing additives on biodegradation of poly (epsilon-caprolactone), *Iranian Polymer Journal*, 9, 221.

Scottish Golf History (s.a.7) [http:// www.scottishgolfhistory.net/tee_term.htm](http://www.scottishgolfhistory.net/tee_term.htm) [2004, March 4].

Shogren, R.L., Fanta, G.F. and Doane, W.M. (1993) Development of starch-based plastics: A re-examination of selected polymer systems in historical perspective, *Starch*, 45, 276 - 280.

Shogren, R.L., Swarson, C.L. and Thompsons, A.R. (1992) Extrudates of corn starch with urea and glycerols: Structure/mechanical property relations, *Starch*, 44 (9), 335 - 338.

Shimao, M., (2001) Biodegradation of plastics, *Biotechnology*, 12: 242 - 247.

Shin, P.K., Kim, M.H. and Kim, J.M. (1997), *Journal of Environmental Polymer Degradation*, 5 (1), 33 - 39.

Sita, C., (2007) *Tensile Properties of Thermoplastic Starch and its Blends with Polyvinyl Butyral and Polyamides*, PhD Thesis, University of Pretoria, South Africa

Sita, C., Burns, M.G., Häßler, R. Focke, W.W. (2006) Tensile properties of thermoplastic starch PVB blends, *Journal of Applied Polymer Science*, 101(3), 1751-1755.

Skoog, D.A. and Leary, J.J. (1992) *Principles of Instrumental Analysis*, 4th ed., Saunders College Publishing, pp 357 - 381.

Swift, G. and Glass, J.E. (1990) Degradability of commodity plastics and speciality polymers: An overview, *In: Agricultural and Synthetic Polymers Biodegradability and Utilization*, American Chemical Society Press, Washington, D.C., Chapter 1, pp. 2 - 12.

The Starch Granule (s.a.8), <http://www.eco-foam.com/processing.asp> [2004, February 19].

Technical committee standards list (s.a.9)

<http://www.iso.ch/iso/en/stddevelopment/tc/tclist>, [2004, March 4].

Van Soest, J.J.G. and Vliegthart J.F.G. (1997). Crystallinity in starch plastics: Consequences for material properties, *Tibtech*, 15, 123 - 125.

Van Soest, J.J.G., Hulleman, S.H.D., De Wit, D. and Vliegthart, J.F.G. (1996a) Changes in the mechanical properties of thermoplastic potato starch in relation with changes in B-type crystallinity, *Carbohydrate Polymers*, 29, 225 - 232.

Van Soest, J.J.G., De Wit, D. and Vliegthart, J.F.G. (1996b) Mechanical properties of thermoplastic waxy maize starch, *Journal of Applied Polymer Science*, 61, 1927 - 1937.

Van Soest, J.J.G., Benes, K. and De Wit, D. (1996c) The influence of starch molecular mass on the properties of extruded thermoplastic starch, *Polymer*, 37 (16), 3543 - 3552.

Williams, K.L. (1987) *An Introduction to X-Ray Spectrometry*, Allen and Unwin, pp 1-110.

Webber, C.J., (2000) "Biobased packaging materials for the food industry", Report, Department of Dairy and Food Science, The Royal Veterinary and Agricultural University, Rolighedsvej 30, 1958 Frederiksberg C, Denmark.

Zobel, H.F. (1988) Molecules to granules: A comprehensive starch review, *Starch*, 40 (2), 44 - 50.

APPENDICES

APPENDIX A: EXTRUSION

Table A1: Sample's compositions

Sample Number and Name	Composition	Mass % of the ingredients
Golf Tees		
1/ U20/Hi20 dumb bell shape	U/Hi/SGPE/St.Ac	20/20/50/10
2/ U20/Hi20 golf tee shape	U/Hi/SGPE/St.Ac	20/20/50/10
3/ U40 dumb bell shape	U/SGPE/St.Ac	40/50/10
4/ U40 golf tee shape	U/SGPE/St.Ac	40/50/10
Seedling Trays		
5/ TPS 15G	Hi/G/W/Si/St.Alc.	66/15/15/3/1
6/ TPS 30G	Hi/G/W/Si/St.Alc	61/30/5/3/1
7/ TPS Eu	TPS15G/Eu2138/U	80/20/2(on top)
8/ TPS EMS	TPS15G/EMS/U	80/20/2(on top)
9/ TPS PVB	TPS30G/PVB/U/EVA	78/22/2(on top)/3(on top)

U - Urea

Hi - Hi Maize Starch

SGPE /PBSA– Sky Green Polyester

St. Alc. – Stearic Alcohol

St.Ac. –Stearic Acid

Si - Precipitated Silica

TPS 15G – TPS containing 15 wt%Glycerol

TPS 30G – TPS containing 30 wt% Glycerol

TPS Eu – blend of TPS 15G and Euremelt 2138

TPS EMS – blend of TPS 15G and EMS

TPS PVB – blend of TPS 30G and PVB

Table A2: Extrusion of Seedling trays compositions

- TPS 15G and TPS 30G were prepared at twin screw extruder Berstoff
- The blends of TPS and PVB, Euremelt 2138 and EMS were prepared at CTM extruder

Sample	Composition	Mass of ingredients (%)	Temp profile (°C)	Speed (rpm)	Torque (amps)
5/TPS 15G	Hi/G/W/Si/St Alc	66/15/15/3/1	Set 100	100	20
6/TPS 30G	Hi/G/W/Si/St.Alc	61/30/5/3/1	Set 100	100	20
7/TPS Eu	TPS15G/E2130/U	80/20/2	103d/130/130/116	25-30	~6
8/TPS EMS	TPS15G/EMS/U	80/20/2	103d/130/130/116	25-30	~6
9/TPS PVB	TPS30G/PVB/U/EVA	78/22/2/3	103d/130/130/116	25-30	~7

d – temperature at the die

% - Percentage in mass basis

PVB – Poly Vinyl Butyral

Hi - Hi Maize Starch

Eu - Euremelt 2138

EMS – Polyamide EMS

U – Urea

G- Glycerol

°C – temperature in degrees Celsius

St.Alc. – Stearic Alcohol

W - Water

rpm – speed in round per minute

amps – torque in amperes

Si – Precipitated Silica

Sample	Composition	Mass of ingredients (%)	Temp profile (°C)	Speed (rpm)	Torque (amps)	Hall of Speed (m/min)	Feeding Rate (kg/h)
1/U20/Hi20	U/Hi/SGPE/St.Ac	20/20/50/10	Set 120	110	~30	33	20.1
3/U40	U/SGPE/St.Ac	40/50/10	Set 120	140	~25	40	23.7

Table A3: Extrusion characteristics of Golf tees compositions, performed at Berstoff

U – Urea

Hi – Hi-maize Starch

SGPE – Sky Green Polyester

St.Ac – Stearic acid

m/min – meter per minutes speed

% - percentage in mass basis

°C – temperature in degrees Celsius

rpm – rounds per minute speed

amps – torque in amperes

kg/h – kilogram per hour feeding speed

APPENDIX B: INJECTION MOULDING

Table B1: Injection moulding parameters of Seedling trays compositions, performed at Engel

Sample	Characteristics of moulds	Temp profile °C	Inj. pressure (bar)	Inj. speed (mm/s)	Hold on pressure (bar)	Hold on time (sec.)	Cooling time (sec.)	Stroke (mm/g)	Plasticizing speed (%)	Back pressure (bar)
5/TPS 15G	No cooling of mould	N150/150/150/150	180	85	20	5	15	28	50	0
6/ TPS 30G	No cooling of mould	N150/150/150/150	120	50	20	5	15	27	50	0
7/TPS Eu	No cooling and heating of mould	N130/130/125/120	120	50	20	5	15	26	50	0
8/TPS EMS	No cooling and heating of mould	N130/130/125/120	120	50	20	5	15	28	50	0
9/TPS PVB	No cooling and heating of mould	N130/130/125/120	100	50	20	5	15	28	50	0

Notes to Table B1

N – temperature at the nozzle

wt% - percentage in mass basis

°C – temperature in degrees Celsius

mm/s - millimetre per second

sec - time in seconds

bar – pressure in bars

d – mass in grams

Table B2: Injection moulding parameters of Golf Tees compositions, performed at Engel

Sample	Feed	Temp profile °C	Inj. pressure (bar)	Inj. speed (mm/s)	Hold on pressure (bar)	Hold on time (sec.)	Cooling time (sec.)	Stroke mm (g)	Plasticizing speed (%)	Back pressure (bar)
1/U20/Hi20	Easy feed	N130/120/110/ 110	100	5	15	5	20	27.5	50	0
3/U40	Easy feed	N120/110/100/ 80	100	50	20	5	15	26	50	0

U – Urea

Hi – Hi-Maize Starch

SGPE – Sky Green Polyester

N – temperature at the nozzle

wt% - percentage in mass basis

°C – temperature in degrees Celsius

sec- time in seconds

bar – pressure in bars

mm/s – millimetres per second Injection speed

g – mass in grams

APPENDIX C: TENSILE TEST DATA

Table C1: Values obtained from tensile testing of Seedling trays compositions at 60% RH, 30°C for 30 days

Composition	Time in Days	Young's Modulus, (MPa)		Tensile Strength, (MPa)		Elongation at break, (%)		Work at break, (J)	
		Ave	STD Dev	Ave	STD Dev	Ave	STD Dev	Ave	STD Dev
5/TPS 15G	1	155.03	27.13	8.71	0.72	32.36	2.52	6.65	0.75
	7	199.10	9.55	9.90	0.27	35.79	2.36	8.58	0.64
	14	217.78	4.19	10.42	0.44	30.26	4.07	7.70	1.40
	30	175.57	10.01	8.97	0.33	31.18	1.29	6.52	0.22
6/TPS 30G	1	34.92	5.52	2.67	0.01	32.77	1.25	1.91	0.04
	7	27.43	0.86	2.04	0.03	24.17	0.70	1.07	0.05
	14	30.23	3.23	2.01	0.21	20.23	3.43	0.87	0.23
	30	33.97	3.30	1.74	0.02	14.28	0.32	0.52	0.02
7/TPS Eu	1	52.21	5.32	3.64	0.14	37.31	3.64	3.09	0.40
	7	96.46	6.06	5.43	0.16	35.02	1.07	4.37	0.21
	14	111.29	13.29	6.02	0.23	34.70	1.38	4.80	0.41
	30	127.43	9.08	6.55	0.28	31.08	2.41	4.86	0.42
8/TPS EMS	1	78.77	5.79	6.43	0.08	46.26	1.14	6.75	0.24
	7	137.66	5.37	8.64	0.18	31.35	2.53	6.13	0.71
	14	147.06	4.47	9.69	0.25	35.98	1.87	8.09	0.63
	30	158.46	7.78	10.03	0.47	38.60	3.01	9.08	1.16
9/TPS PVB	1	13.75	3.09	1.34	0.05	55.53	1.96	1.69	0.05
	7	10.21	0.51	1.14	0.02	49.78	4.54	1.27	0.06
	14	9.55	0.59	1.08	0.04	50.80	2.37	1.19	0.05
	30	12.30	4.07	1.07	0.04	43.88	3.95	1.06	0.11

Notes to Table C2

U – Urea

Hi – Hi-Maize Starch

SGPE/PBSA – Sky Green Polyester

MPa – pressure in mega pascals

% - percentage in mass basis

J – work in Joules

Table C2: Values obtained from tensile testing of Golf tees compositions at 0% RH and 60% RH, for 30 days

Composition	Time in Days	Young's Modulus, (MPa)		Tensile Strength, (MPa)		Elongation at break (%)		Work at break, (J)	
		Ave	STD Dev	Ave	STD Dev	Ave	STD Dev	Ave	STD Dev
1/U20/Hi20	1	240.46	9.45	11.89	0.46	8.54	1.06	1.93	0.43
60% RH , 30C	7	281.90	10.49	12.78	0.37	7.77	0.70	1.88	0.28
	14	298.98	4.67	12.69	0.36	6.82	0.34	1.52	0.16
	30	293.63	6.86	12.97	0.20	7.20	0.58	1.67	0.21
1/U20/Hi20	1	242.16	9.54	12.49	0.15	9.32	0.66	2.19	0.28
0% RH , 25C	7	289.59	8.05	13.20	0.19	7.32	0.34	1.70	0.16
	14	312.63	8.27	13.41	0.57	7.00	0.41	1.57	0.23
	30	314.77	14.41	13.29	0.50	7.61	0.58	1.79	0.20
3/U40	1	270.90	14.39	11.26	2.21	5.75	1.17	0.99	0.41
60% RH , 30C									

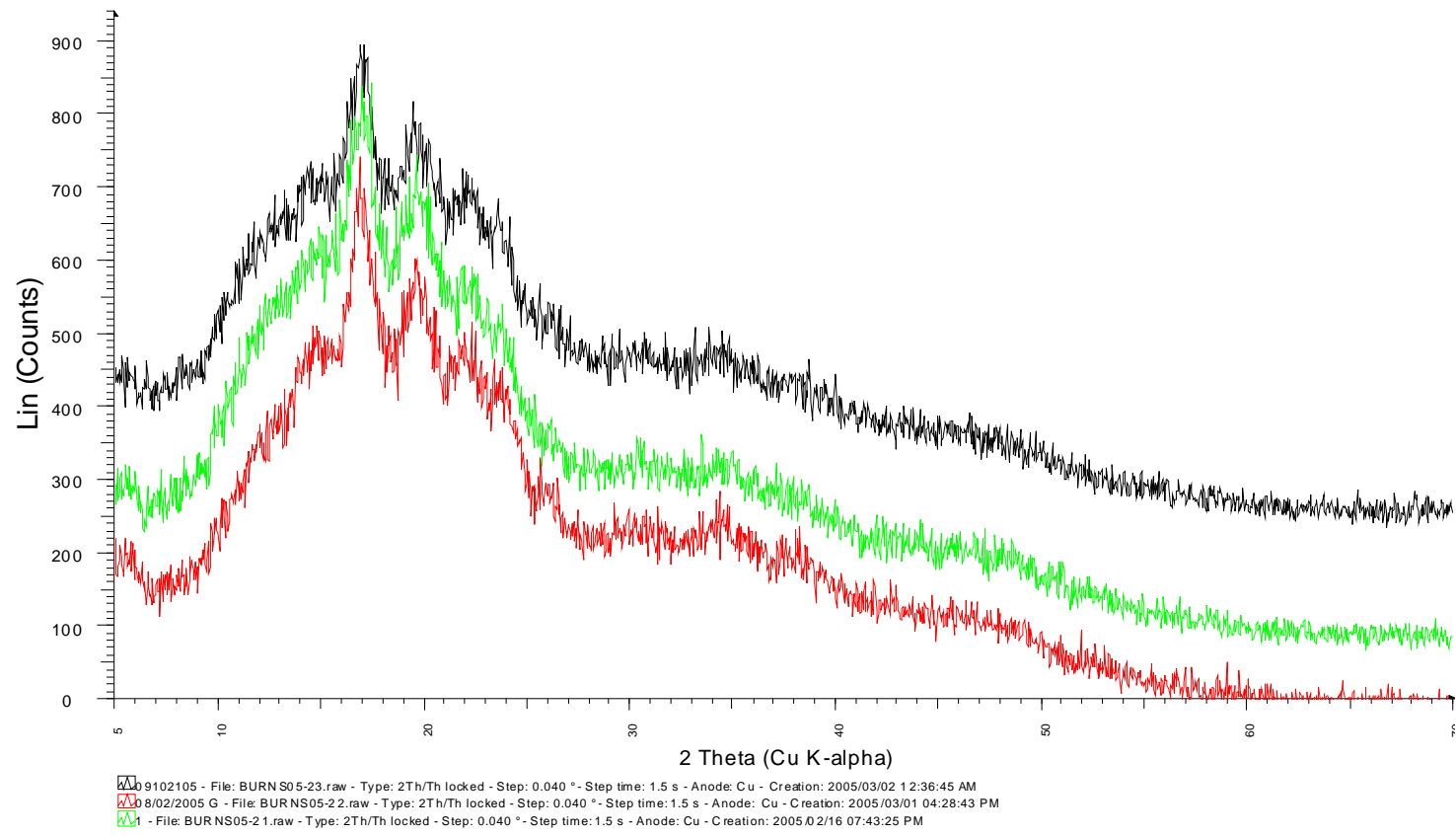
Hi – Hi-Maize Starch

wt% - percentage in mass basis

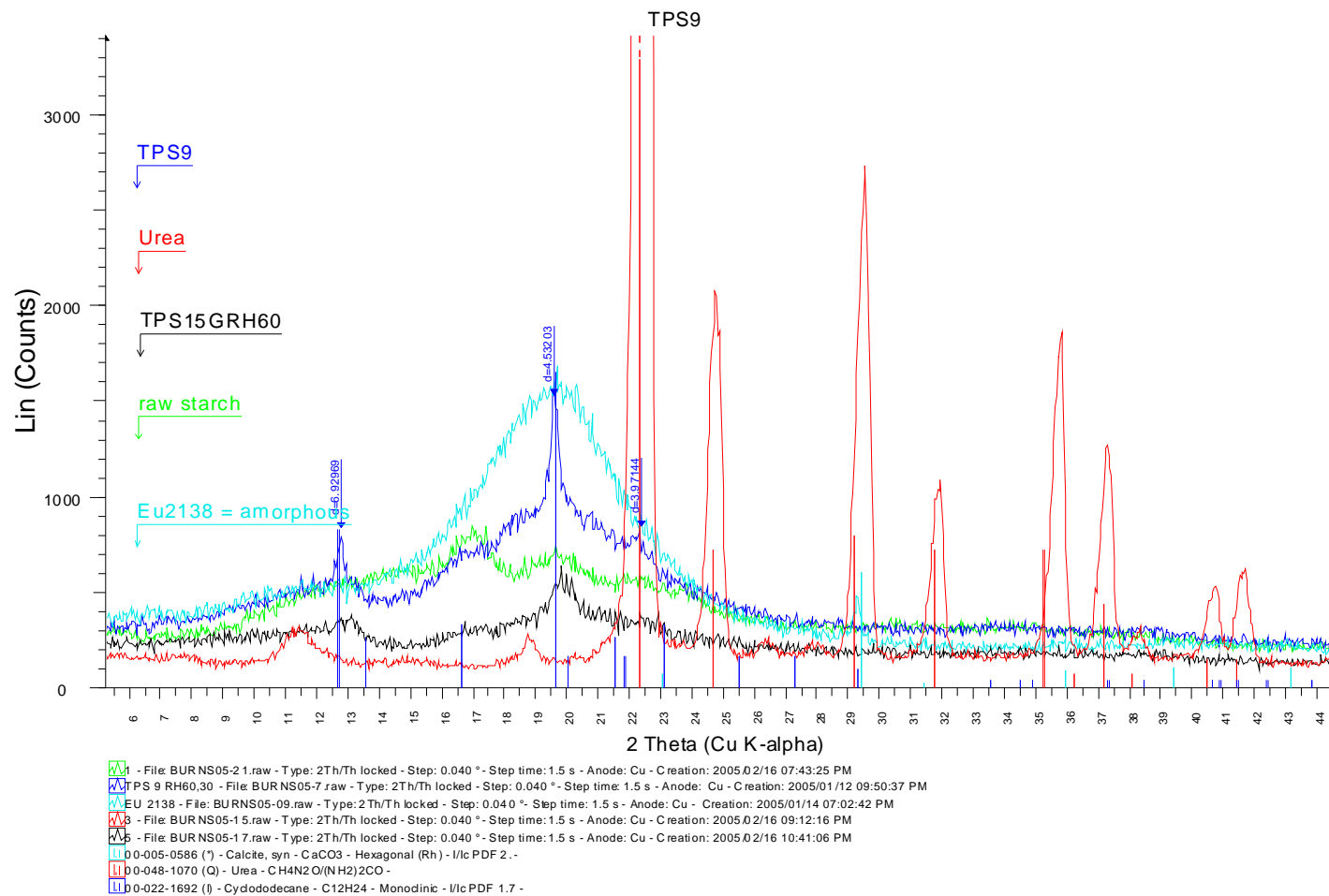
SGPE/PBSA – Sky Green Polyester

J – work in Joules

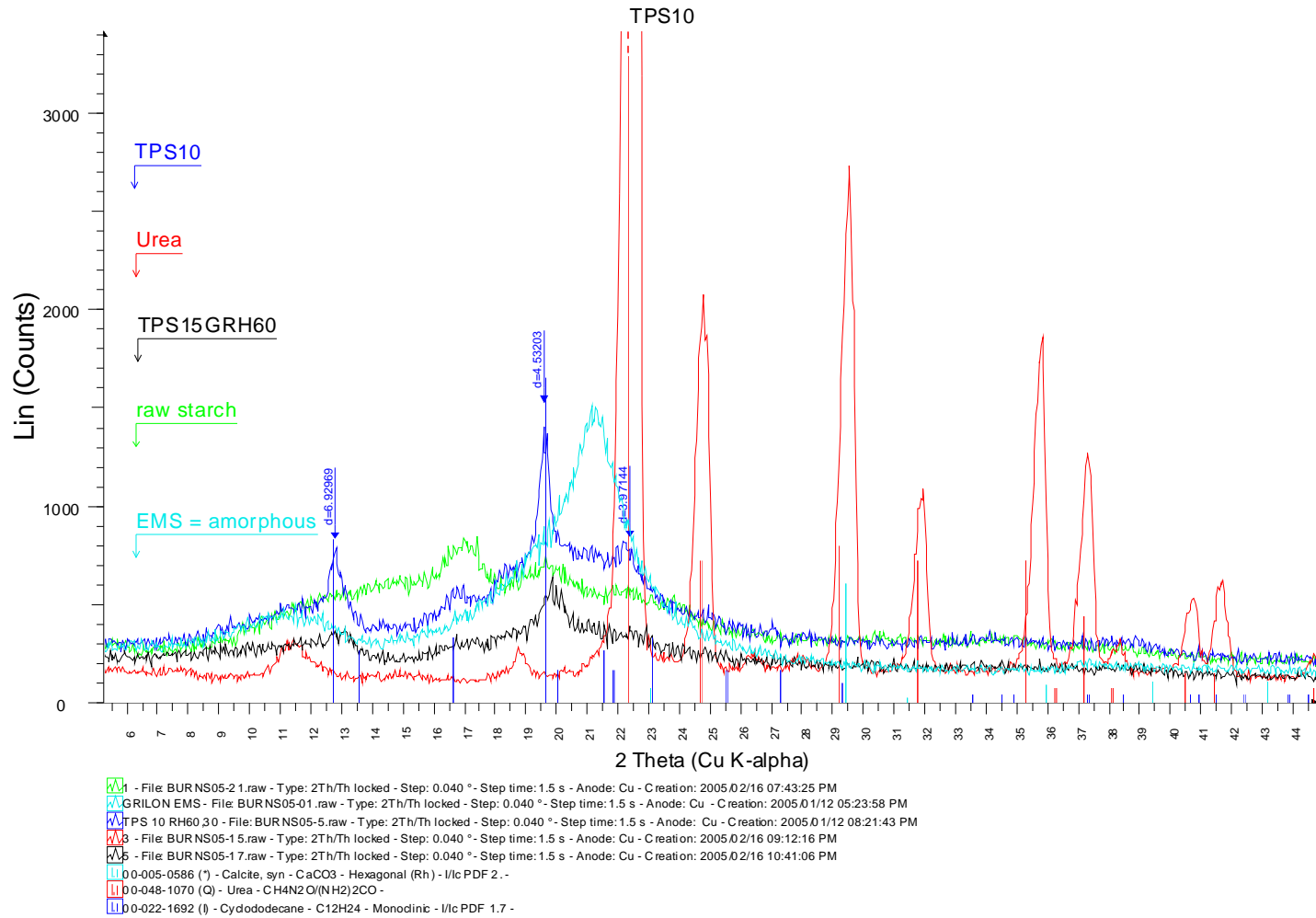
APPENDIX D: XRD SPECTRA



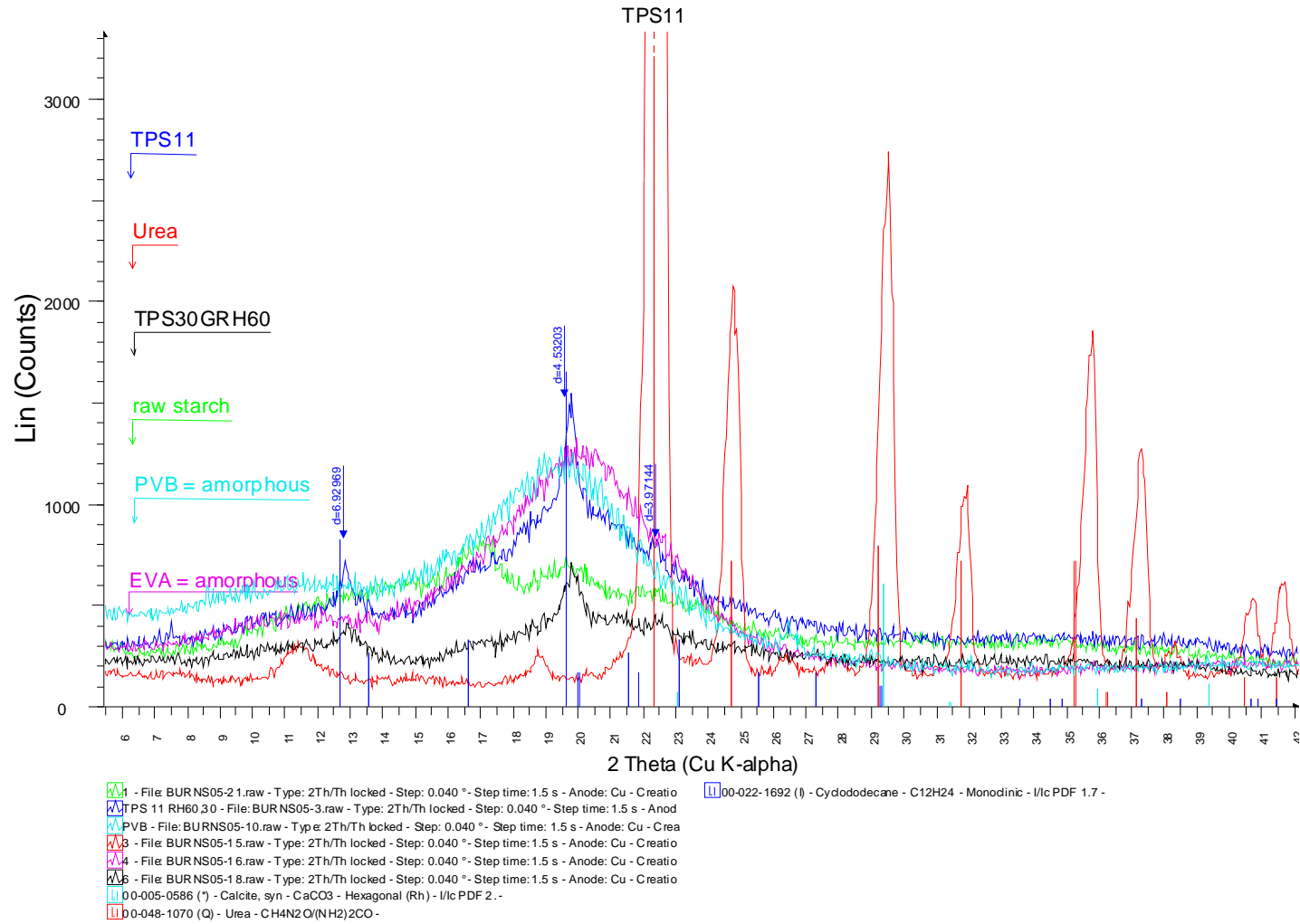
Spectrum D1: Raw Starch diffractogram



Spectrum D2: TPS 9/Eu and raw materials

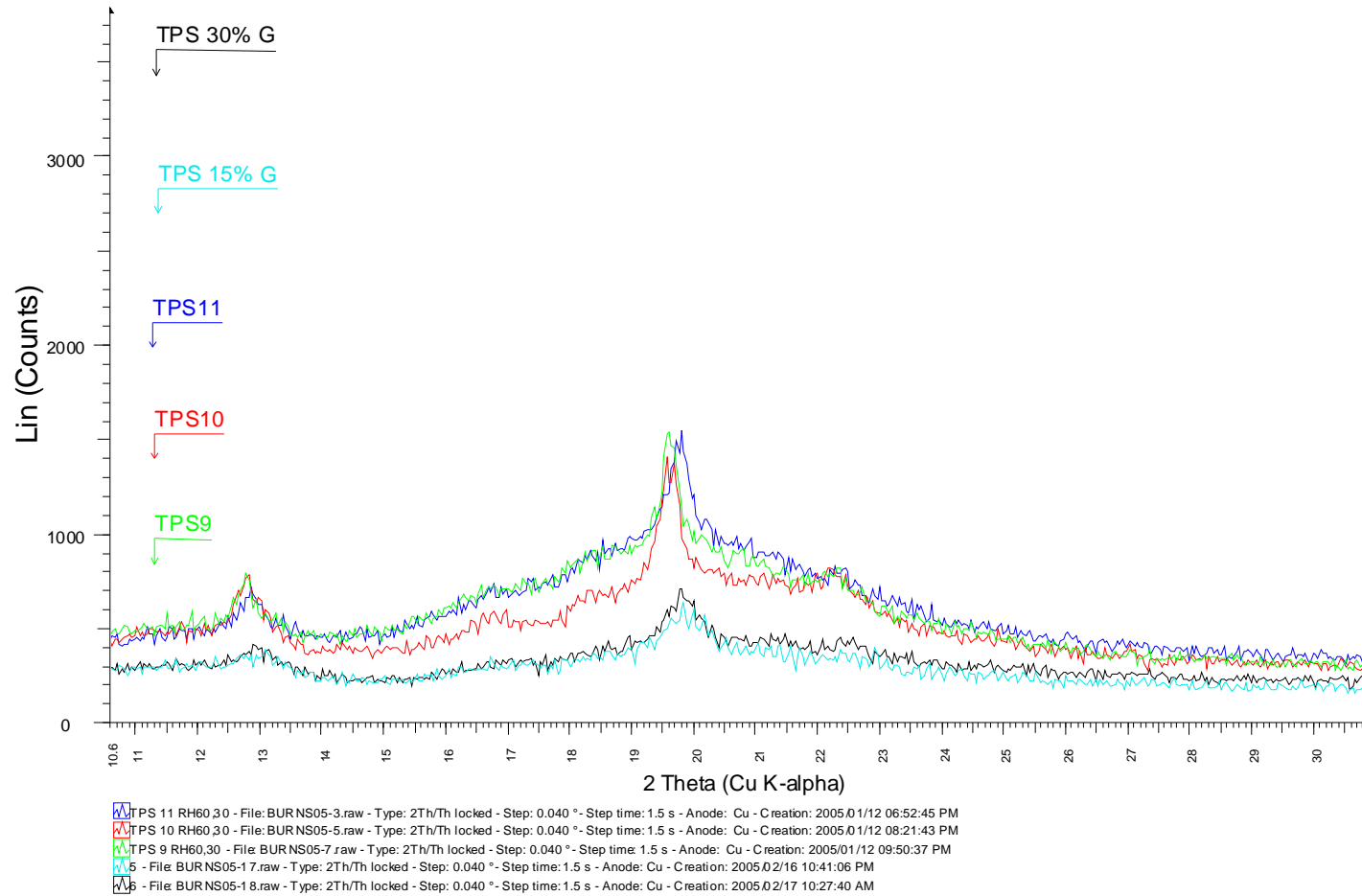


Spectrum D3: TPS 10/EMS and raw materials



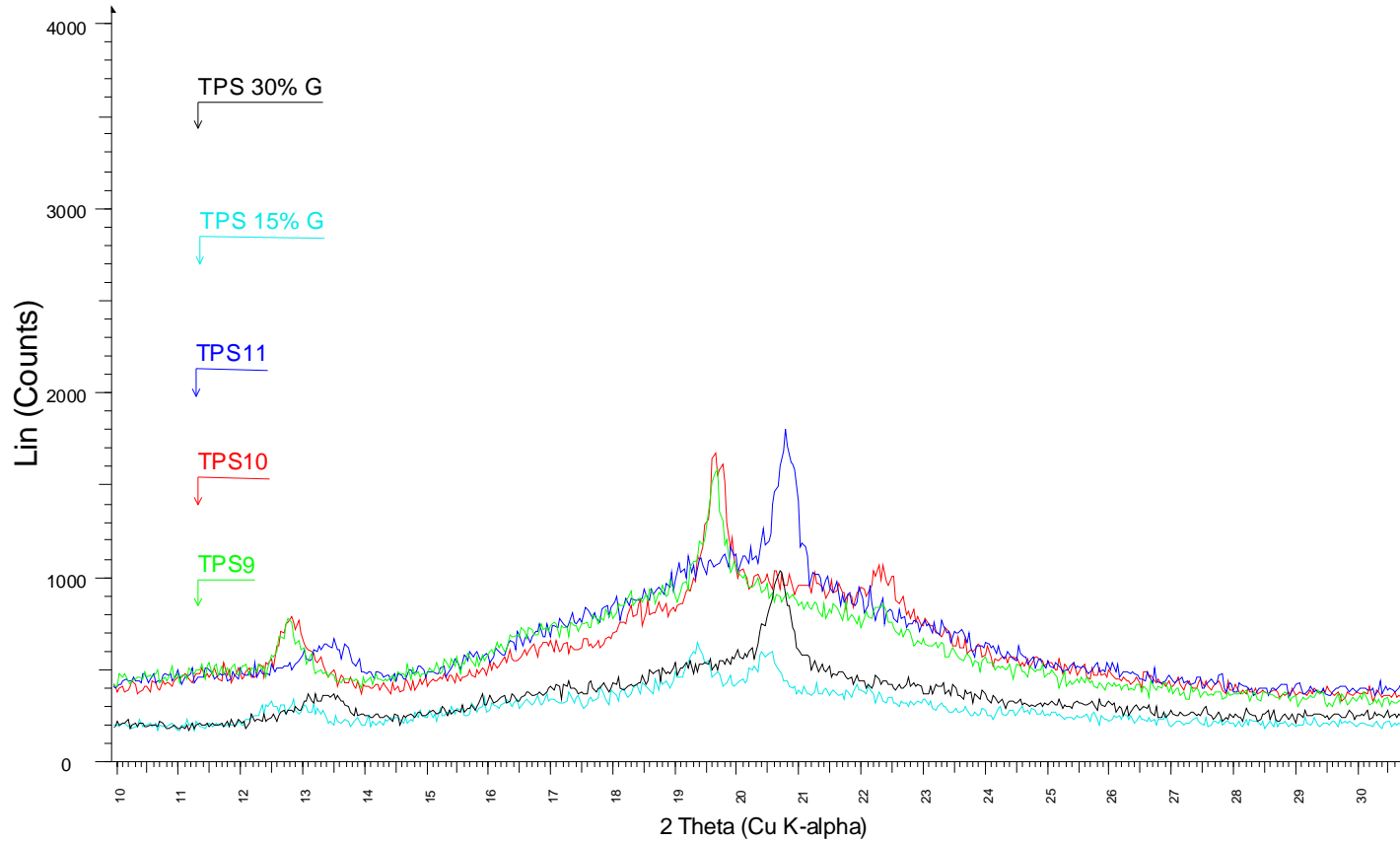
Spectrum D4: TPS 11/PVB and raw materials

TPS 9-10-11 RH60 30C



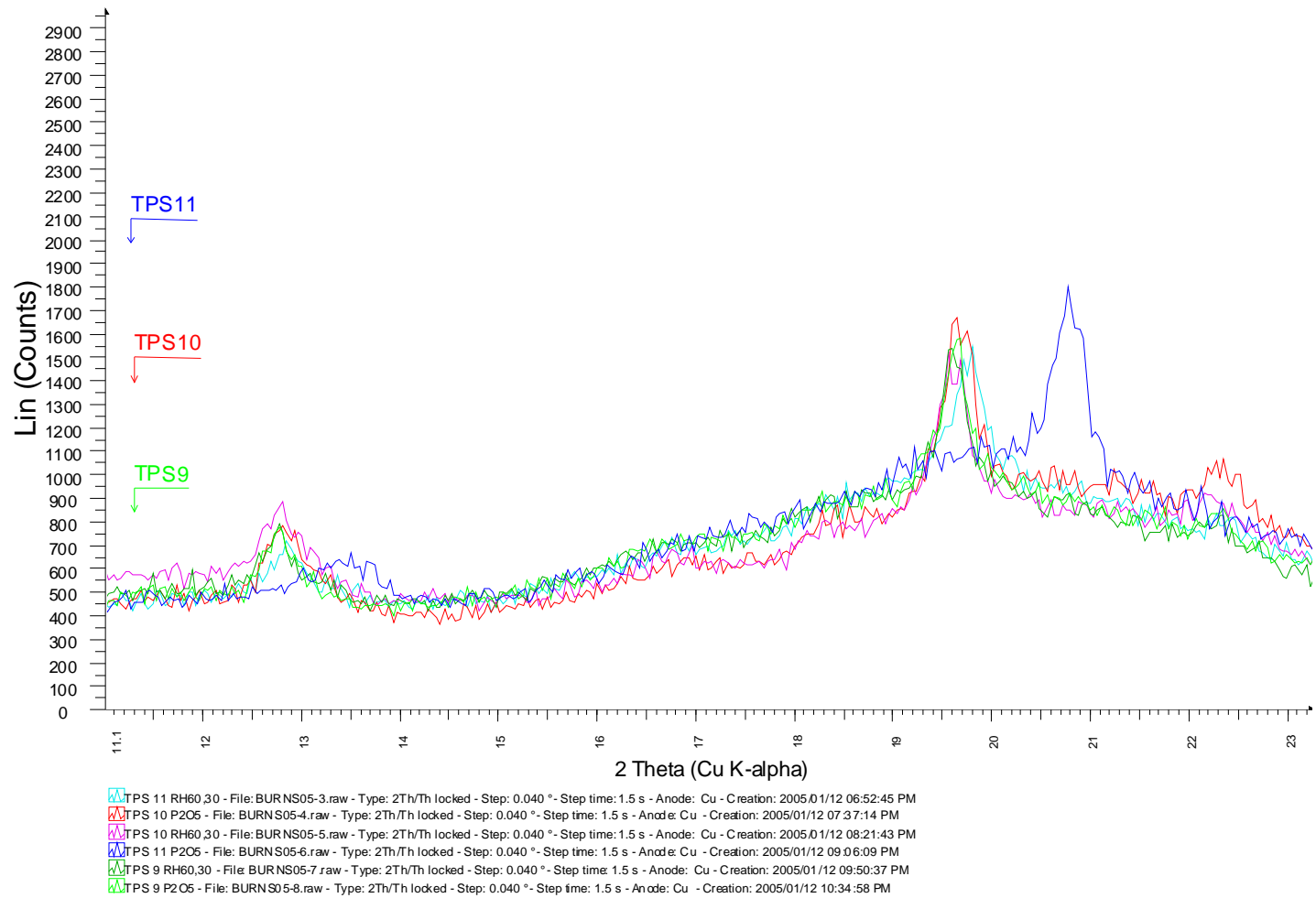
Spectrum D5: TPS 9/Eu, 10/EMS and 11/PVB and TPS 15G, TPS 30G aged at 60% RH, 30C

TPS 9-10-11 P2O5



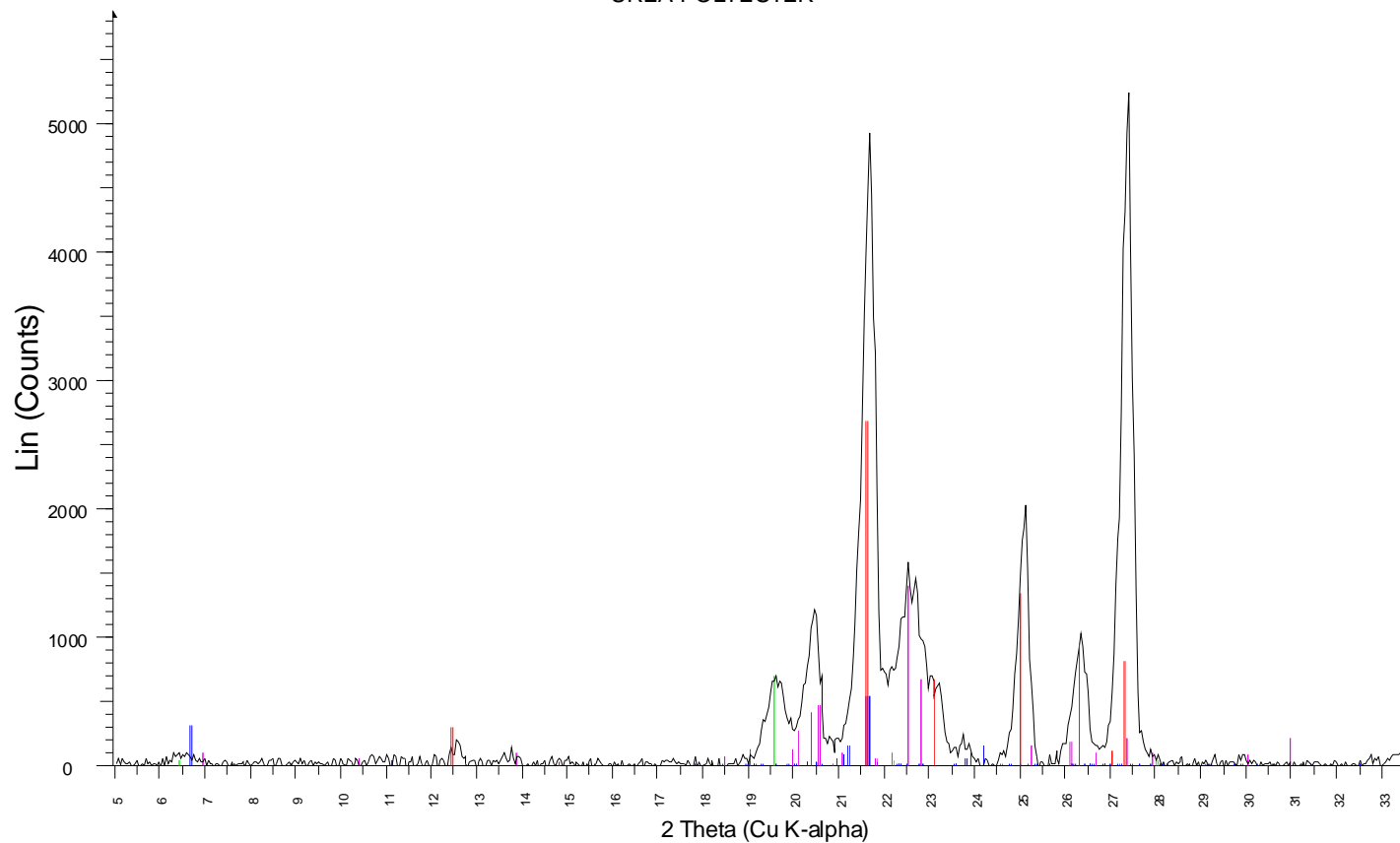
TPS 10 P2O5 - File: BURNS05-4.raw - Type: 2Th/Th locked - Step: 0.040 ° - Step time: 1.5 s - Anode: Cu - Creation: 2005/01/12 07:37:14 PM
TPS 11 P2O5 - File: BURNS05-6.raw - Type: 2Th/Th locked - Step: 0.040 ° - Step time: 1.5 s - Anode: Cu - Creation: 2005/01/12 09:06:09 PM
TPS 9 P2O5 - File: BURNS05-8.raw - Type: 2Th/Th locked - Step: 0.040 ° - Step time: 1.5 s - Anode: Cu - Creation: 2005/01/12 10:34:58 PM
10 - File: BURNS05-25.raw - Type: 2Th/Th locked - Step: 0.040 ° - Step time: 1.5 s - Anode: Cu - Creation: 2005/04/22 10:36:18 AM
11 - File: BURNS05-24.raw - Type: 2Th/Th locked - Step: 0.040 ° - Step time: 1.5 s - Anode: Cu - Creation: 2005/04/22 09:51:57 AM






Spectrum D6: TPS 9/Eu, 10/EMS, 11/PVB aged at 0% RH, 25°C



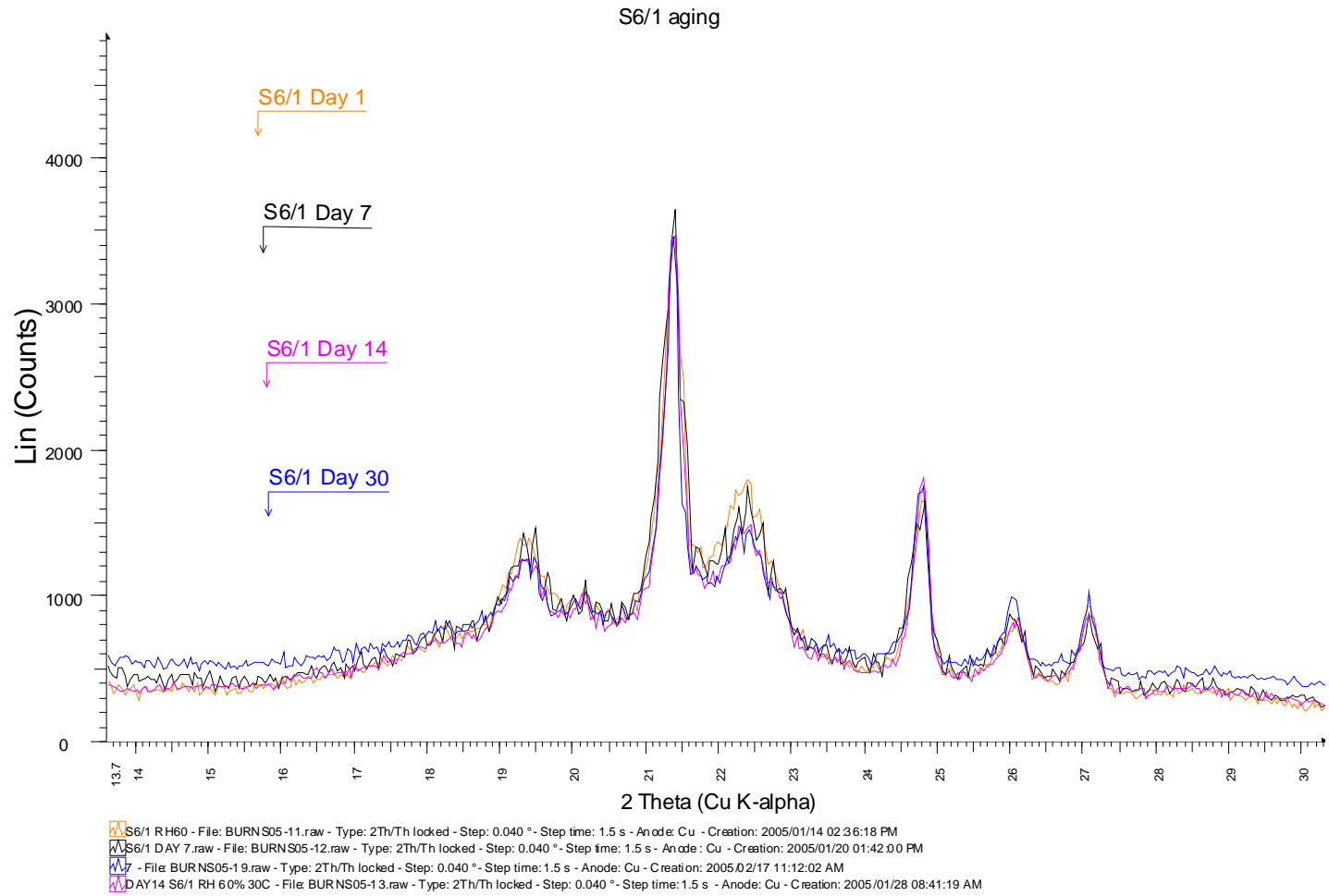
Spectrum D7: TPS 9/Eu, 10/EMS and 11/PVB aged at 60% RH, 30°C and 0% RH, 25°C

UREA POLYESTER



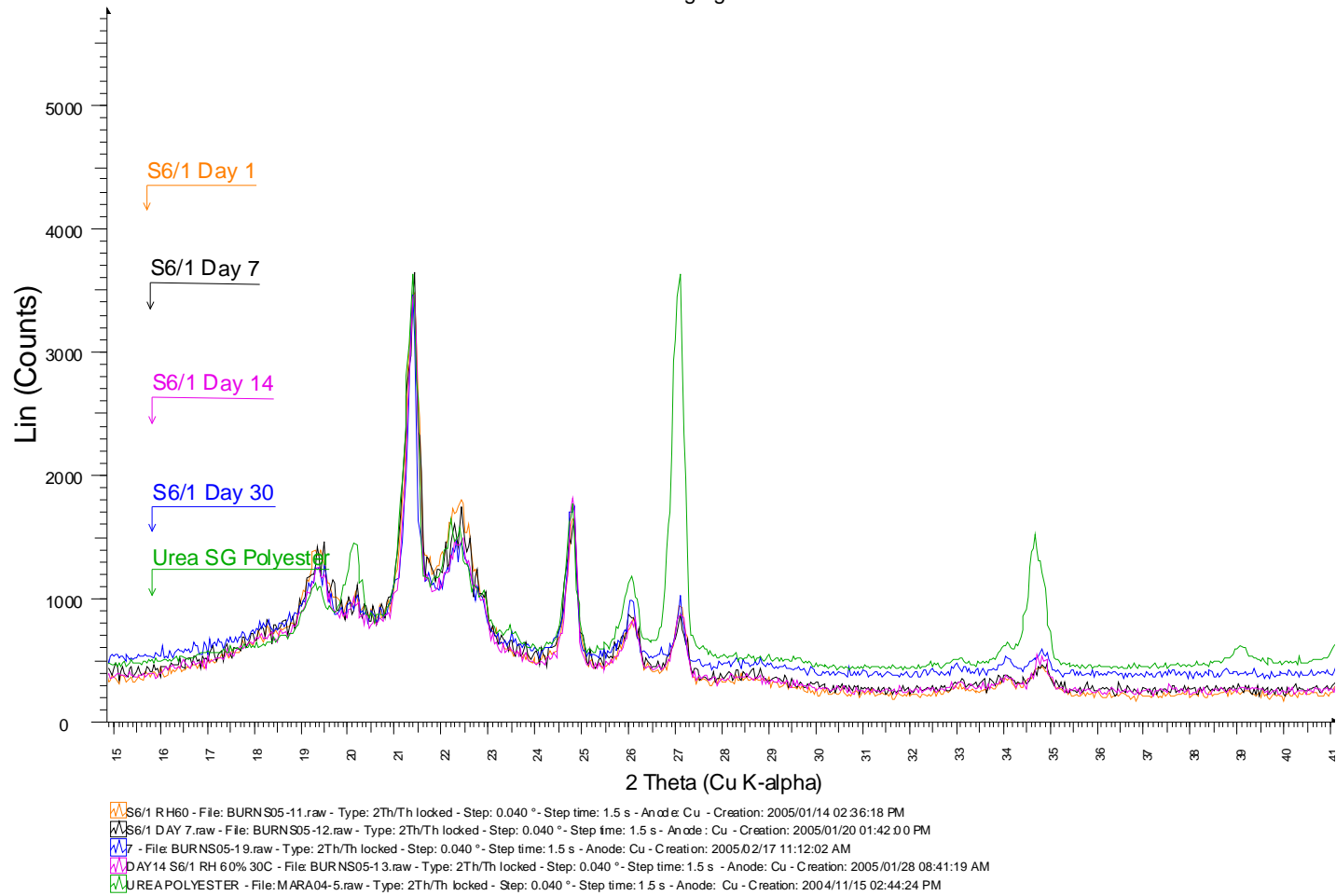
 UREA POLYESTER - File: MARA04-5.raw - Type: 2Th/Th locked - Start 5.000 ° - End: 70.000 ° - Step: 0.0 40 ° - Step time: 1.5 s - Anode: Cu - X-Offset: 0.0 00 - Displ.: 0. mm - Creation: 2004/11/15 02:44:24 PM
 00-034-1766 (N) - Polyethyleneurea complex - C₁₄H₂₄N₂O₆/(CH₂)₈.76-6CO(NH₂)₂ - Hexagonal -
 00-038-1923 (*) - Stearic acid - C₁₈H₃₆O₂ - Monoclinic -
 00-049-2268 (Q) - Pd₂(N-ethyl-bisbenzylamine 4,4'-diimido-diphenylethane) - (C₃₄H₂3N₃O₆)n/[N(CO)₂(C₆H₃)(CO)(C₂H₅CO)(C₆H₃)(CO)₂N(C₆H₄CH₂CH₂ -
 00-051-1902 (*) - alpha-Glutamic acid - C₅H₈O₄ - Monoclinic -

Spectrum D8: U40



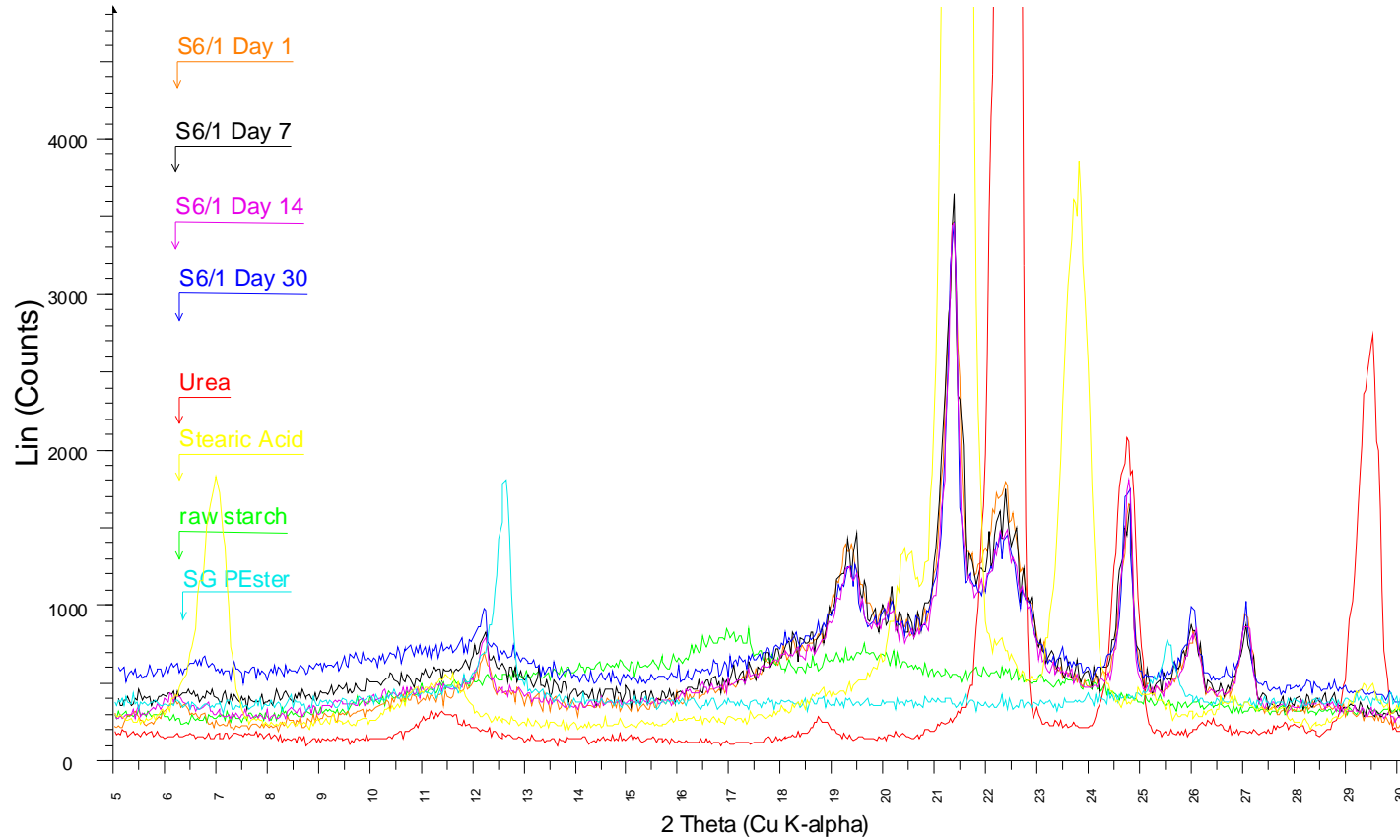
Spectrum D9: U20/Hi20 ageing at 60% RH, 30°C

S6/1 aging



Spectrum D10: U40 and U20/Hi20 aged spectrums

S6/1



■ 1 - File: BURNS05-21.raw - Type: 2Th/Th locked - Step: 0.040 ° - Step time: 1.5 s - Anode: Cu - Creation: 2005/02/16 07:43:25 PM
■ S6/1 R H60 - File: BURN S05-11.raw - Type: 2Th/Th locked - Step: 0.040 ° - Step time: 1.5 s - Anode: Cu - Creation: 2005/01/14 02:36:18 PM
■ S6/1 DAY 7.raw - File: BURNS05-12.raw - Type: 2Th/Th locked - Step: 0.040 ° - Step time: 1.5 s - Anode: Cu - Creation: 2005/01/20 01:42:00 PM
■ 2 - File: BURNS05-14.raw - Type: 2Th/Th locked - Step: 0.040 ° - Step time: 1.5 s - Anode: Cu - Creation: 2005/02/16 08:27:50 PM
■ 3 - File: BURNS05-15.raw - Type: 2Th/Th locked - Step: 0.040 ° - Step time: 1.5 s - Anode: Cu - Creation: 2005/02/16 09:12:16 PM
■ 7 - File: BURNS05-19.raw - Type: 2Th/Th locked - Step: 0.040 ° - Step time: 1.5 s - Anode: Cu - Creation: 2005/02/17 11:12:02 AM
■ DAY14 S6/1 RH 60% 30C - File: BURNS05-13.raw - Type: 2Th/Th locked - Step: 0.040 ° - Step time: 1.5 s - Anode: Cu - Creation: 2005/01/28 08:41:19 AM
■ SG PESTER - File: BURNS04-02.raw - Type: 2Th/Th locked - Step: 0.040 ° - Step time: 1.5 s - Anode: Cu - Creation: 2004/12/09 03:18:40 PM

Spectrum D11: U20/Hi20 and raw materials

APPENDIX E: COMPOSTABILITY TENSILE TEST DATA

Table E1: Observed compostability parameters according to ASTM G160

Parameter	Days measured	Result
pH		
Container 1(Golf Tees samples)	Day 1	7.3
	Day 60	7.5
Container 2(Seedling Trays samples)	Day 1	7.0
	Day 60	7.5
Moisture of soil, mass%		
Container 1(Golf Tees samples)	Day 1	29.94
	Day 30	34.15
	Day 60	20.07
Container 2(Seedling Trays samples)	Day 1	37.18
	Day 30	30.49
	Day 60	24.99
Material Tensile Strength, MPa		
	Before burial	224.31
	After three days	123.00

Table E2: Values obtained from tensile testing of Seedling trays compositions during composting for 60 days

Composition	Time in Days	Young's Modulus, (MPa)		Tensile Strength, (MPa)		Elongation at break (%)		Work at break, (J)	
		Ave	STD Dev	Ave	STD Dev	Ave	STD Dev	Ave	STD Dev
5/TPS 15G	0	252.79	19.59	11.53	0.36	25.71	2.91	7.19	1.08
6/TPS 30G	0	30.68	3.17	2.18	0.02	20.12	1.28	0.95	0.07
7/TPS Eu	0	129.02	12.88	6.54	0.49	28.17	1.09	4.29	0.58
	7	59.86	21.27	2.46	0.27	15.84	4.71	0.79	0.32
	13	37.79	8.08	1.93	0.19	18.46	1.06	0.71	0.09
	30	28.70	1.97	1.60	0.21	14.18	2.22	0.42	0.13
	45	0.03	0.00	0.00	0.00	11.72	3.06	0.29	0.13
	60	0.01	0.00	0.00	0.00	22.99	9.01	0.26	0.11
8/TPS EMS	0	172.15	9.87	10.42	0.18	28.26	5.25	6.69	1.55
	7	103.95	10.57	5.45	0.61	17.40	2.24	1.92	0.42
	13	83.48	15.84	3.87	0.71	15.66	2.70	1.18	0.35
	30	41.64	18.48	3.09	1.22	17.99	2.45	1.09	0.46
	45	0.07	0.00	0.00	0.00	10.51	2.60	0.62	0.22
	60	0.01	0.00	0.00	0.00	38.98	18.49	0.77	0.40
9/TPS PVB	0	16.78	2.05	1.31	0.01	43.13	1.07	1.28	0.04
	7	30.68	14.53	1.34	0.05	19.53	6.21	0.54	0.17
	13	47.18	13.21	1.17	0.25	10.45	0.00	0.12	0.05
	30	42.66	15.11	1.36	0.39	10.12	4.54	0.15	0.04
	45	0.05	0.00	0.00	0.00	4.45	1.10	0.12	0.04
	60	0.07	0.01	0.00	0.00	8.93	3.52	0.12	0.02

Table E3: of values obtained from tensile testing of Golf tees compositions during composting for 60 days

Composition	Time in Days	Young's Modulus, (Mpa)		Tensile Strength, (MPa)		Elongation at break (%)		Work at break, (J)	
		AVE	STD DEV	Ave	STD Dev	Ave	STD Dev	Ave	STD Dev
1/U20/Hi20	0	292.70	20.59	12.42	0.58	6.75	0.77	1.45	0.28
	7	78.93	9.82	5.52	0.29	16.67	2.75	1.91	0.44
	13	63.10	3.48	5.00	0.20	13.81	1.55	1.29	0.18
	30	69.99	6.48	4.73	0.48	9.60	0.83	0.83	0.19
	45	0.08	0.01	0.00	0.00	6.91	0.46	0.52	0.06
	60	0.08	0.01	0.00	0.00	6.74	0.95	0.46	0.11
3/U40	0	270.90	14.39	11.26	2.21	5.75	1.17	0.99	0.41
	7	82.70	3.44	6.55	0.66	14.90	2.10	1.28	0.22
	13	47.45	4.13	4.41	0.92	15.14	1.75	1.05	0.39
	30	52.80	14.75	2.01	0.61	5.56	1.53	0.18	0.08
	45	0.07	0.03	0.00	0.00	4.45	1.48	0.16	0.10
	60	0.07	0.01	0.00	0.00	3.78	0.88	0.12	0.06

d – temperature at the die

U – Urea

G – Glycerol

St.Ac – Stearic Acid

wt% - Percentage in mass basis

°C – temperature in degrees Celsius

rpm – speed in round per minute

J – work in Joules

APPENDIX F: SEM

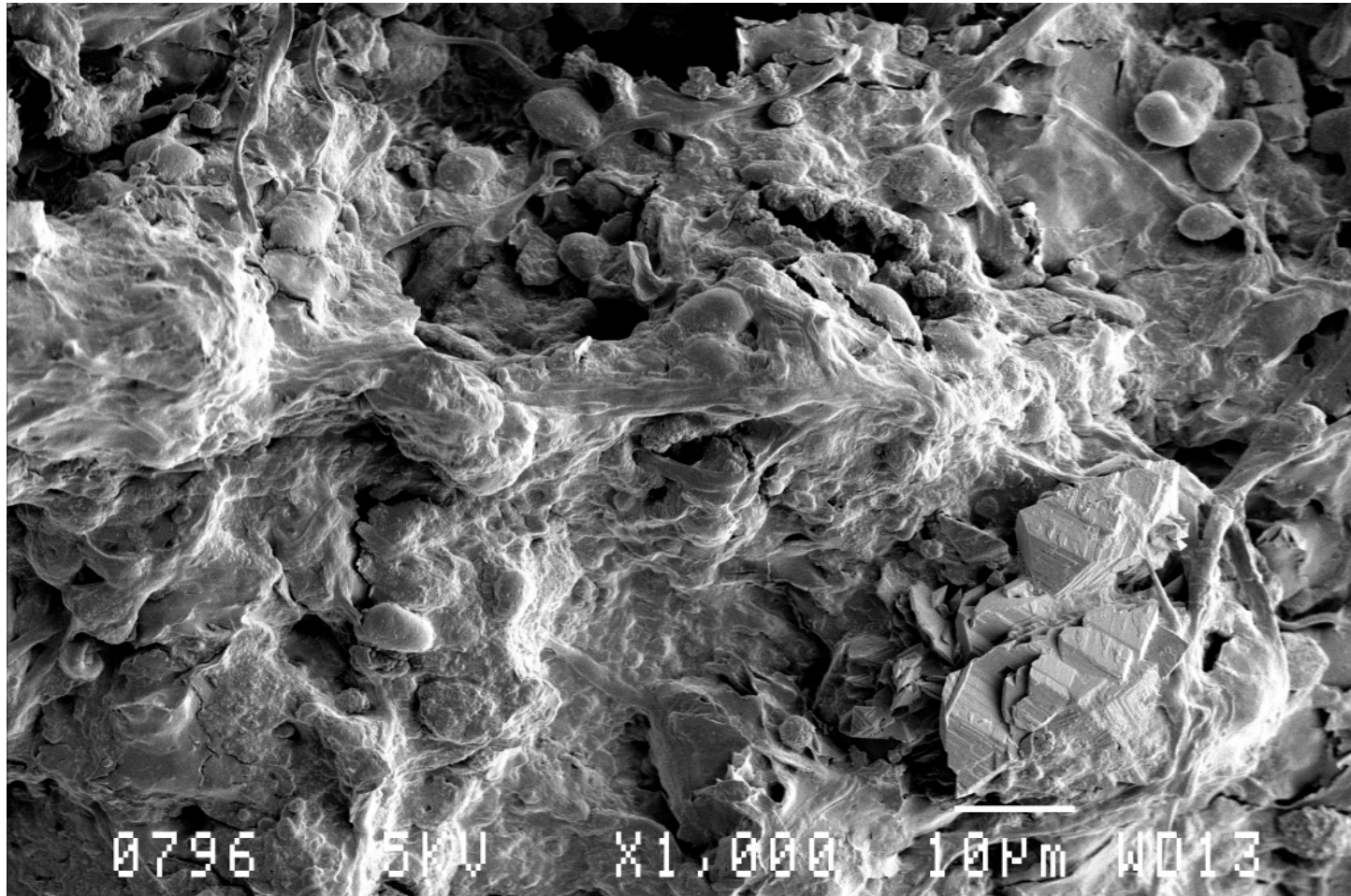


Figure F1: Microphotograph of TPS 15G crystal structures: crystals of vitamins, produced by microorganisms, soil or sand structures. Picture taken at day 45 of composting inside the cut specimen at magnification X1000

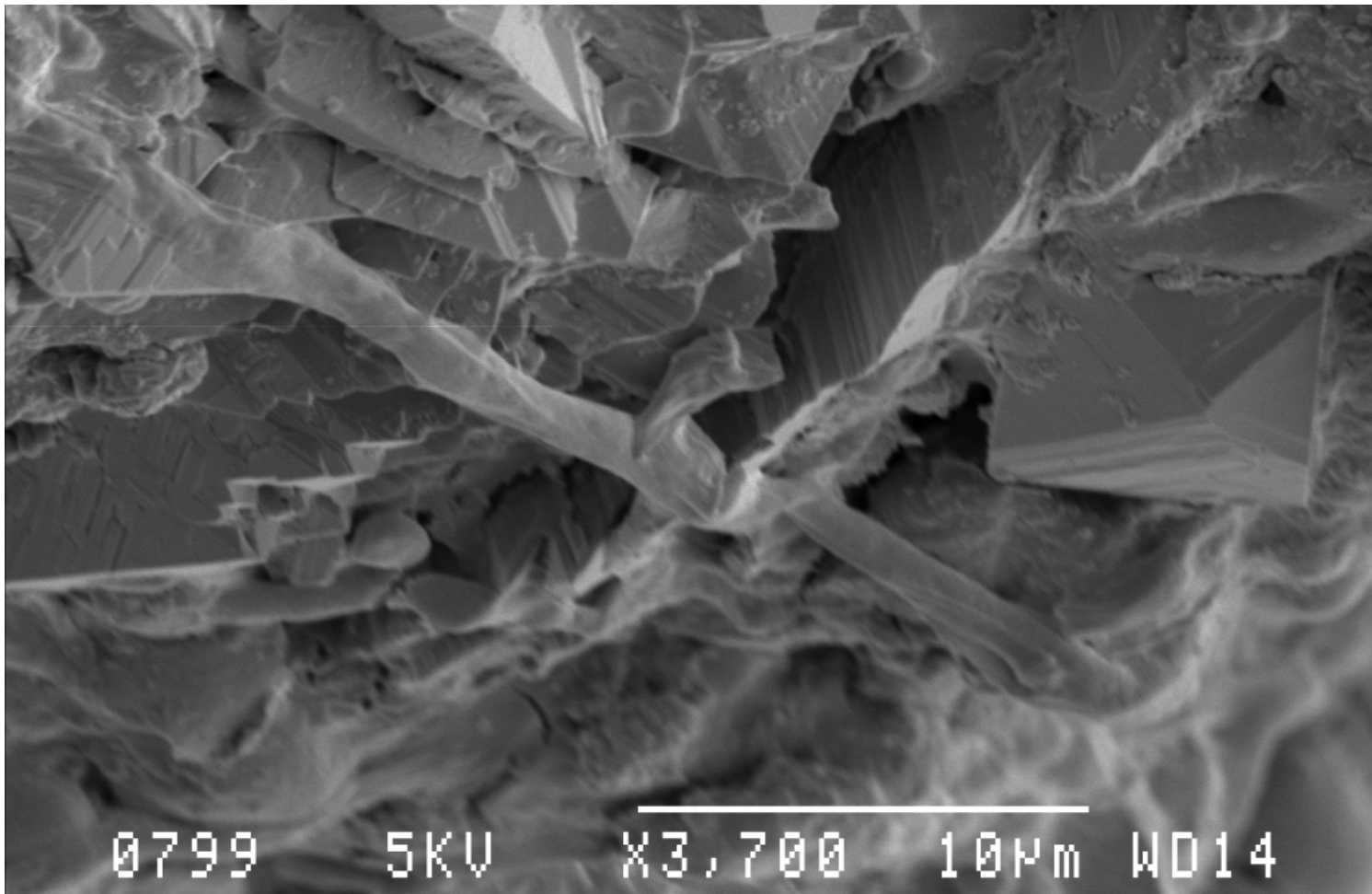


Figure F2: Microphotograph of TPS 15G collapsed microfibrils and crystal structure. Picture taken at day 45 of composting, inside the cut specimen, at magnification x3 700

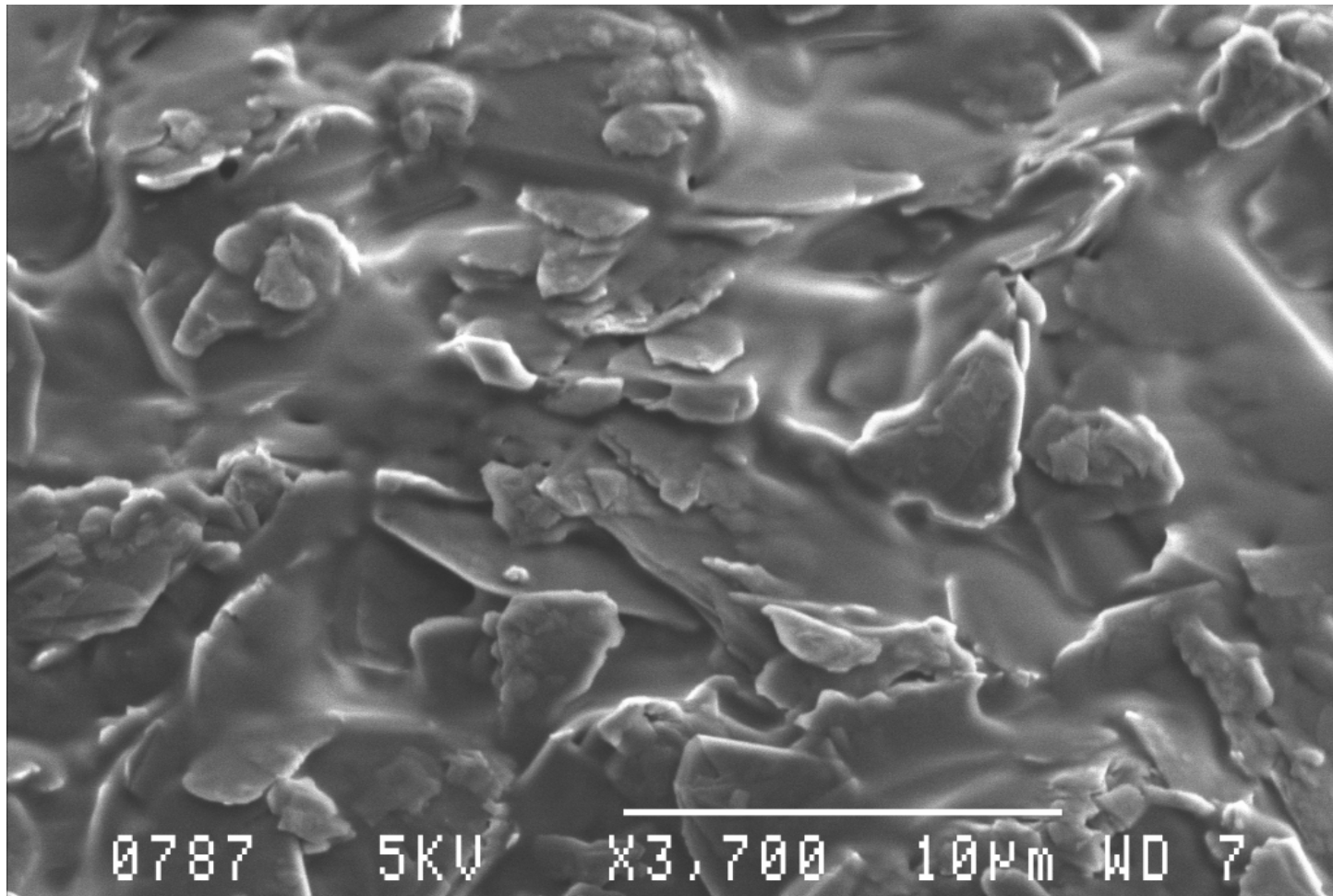


Figure F3: Microphotograph of TPS 30G microorganism activity, slime effect. Photo taken from the outside degradation layer at day 13 of the computability test. Magnification x3 700.

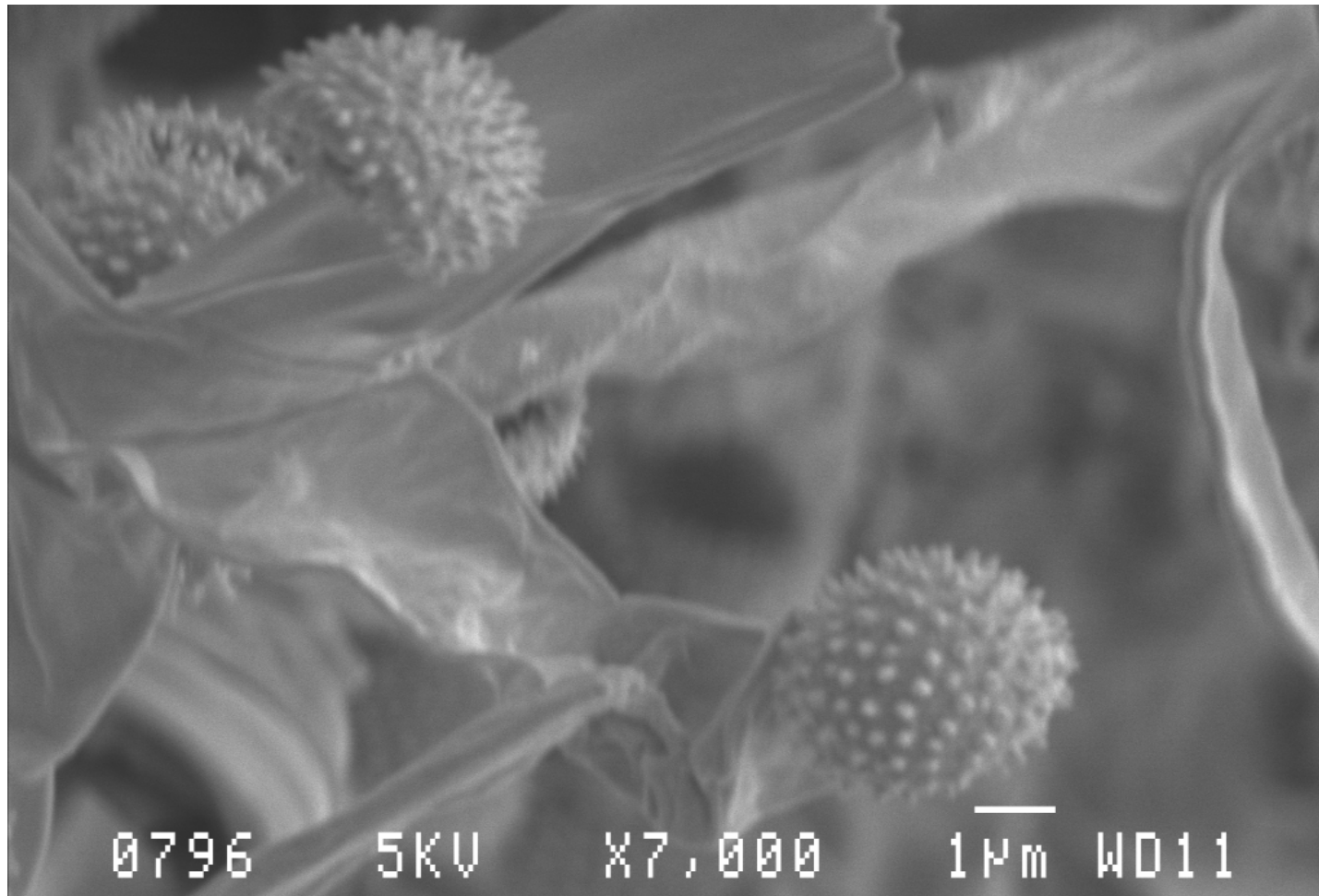


Figure F4: Microphotograph TPS Eu spores. Picture taken at day 13 of compostability test, outside degradation layer at magnification x7 000.

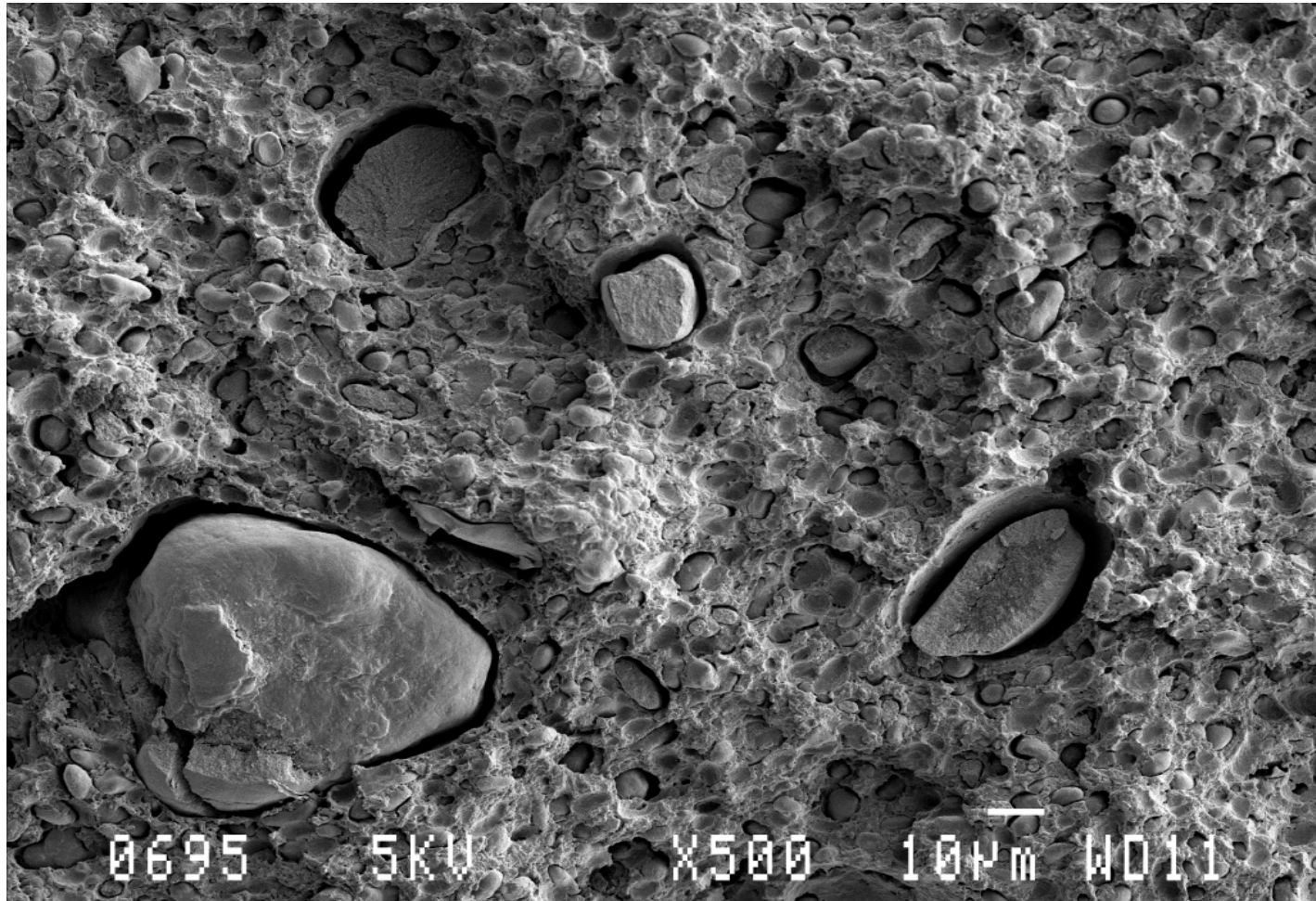


Figure F5: Broken Starch granule in TPS EMS bottom right. Photo taken at day 7 of the compostability test at magnification x500, inside of the degradation layer

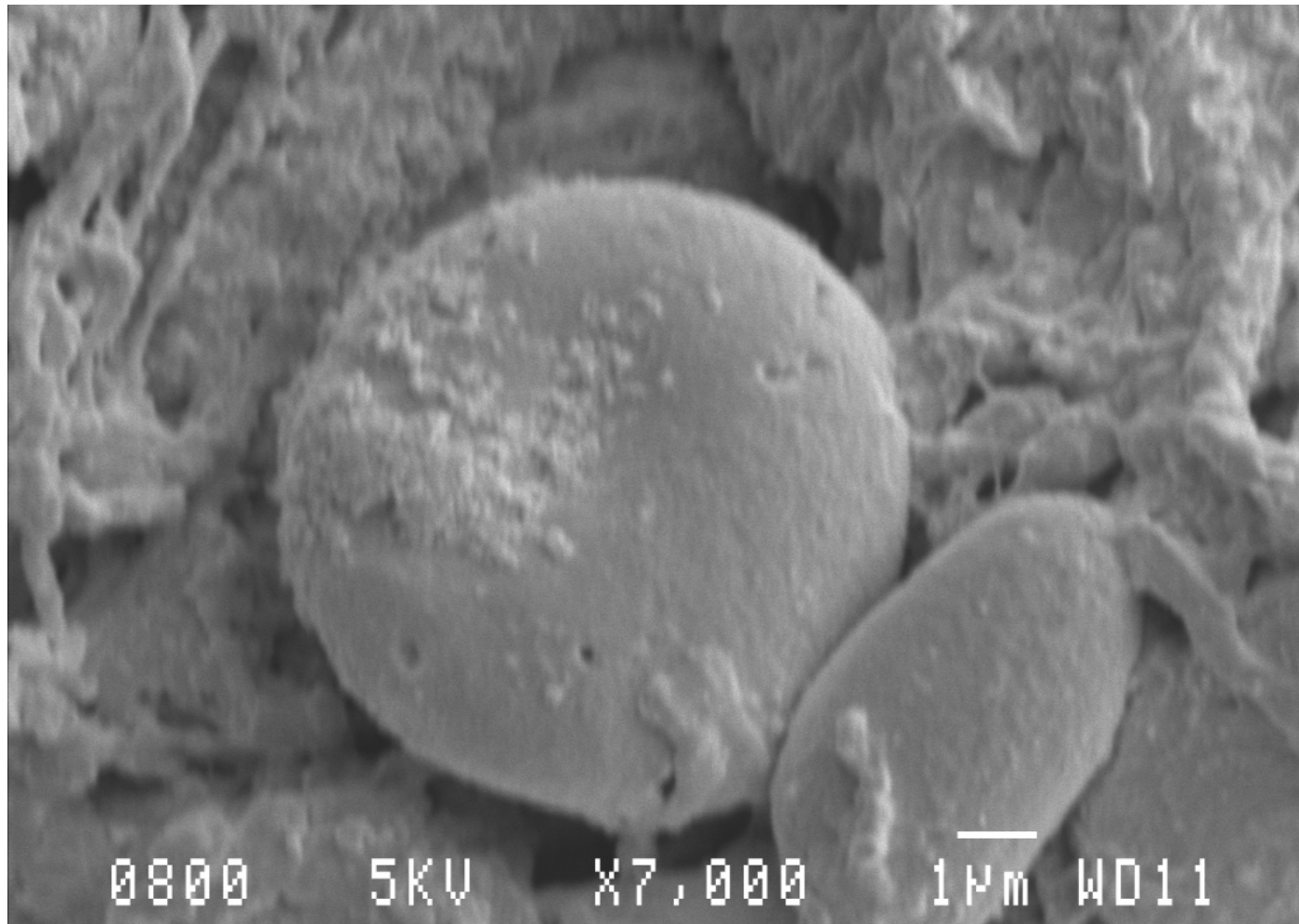


Figure F6: Start of the degradation/pitting at the starch granule in TPS EMS. Photo taken from the inside degradation layer, day 13 of the degradation process and magnification x7 000

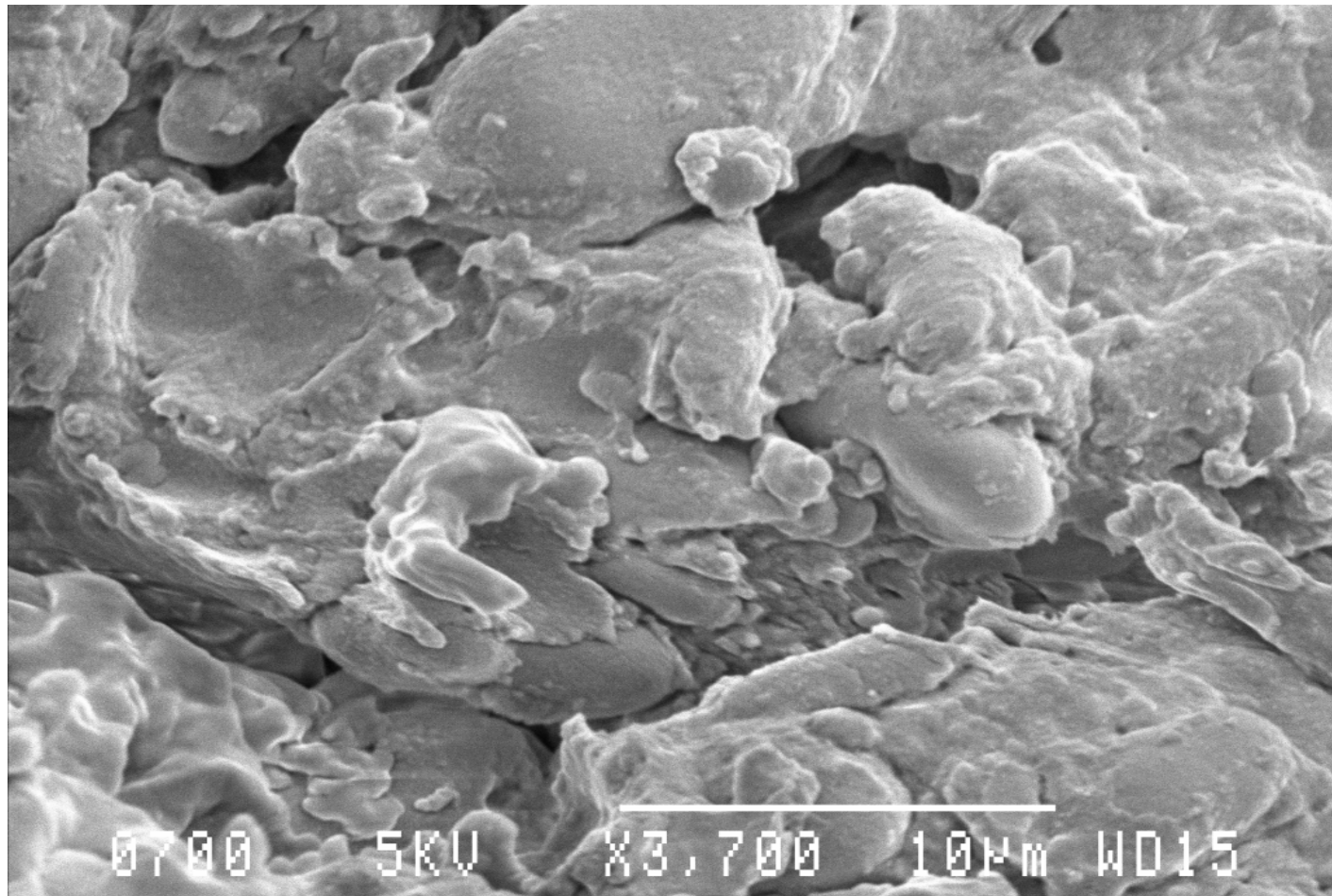


Figure F7: Slime effect in TPS PVB. Photo taken at day 7 of the composting at x3 700 magnification

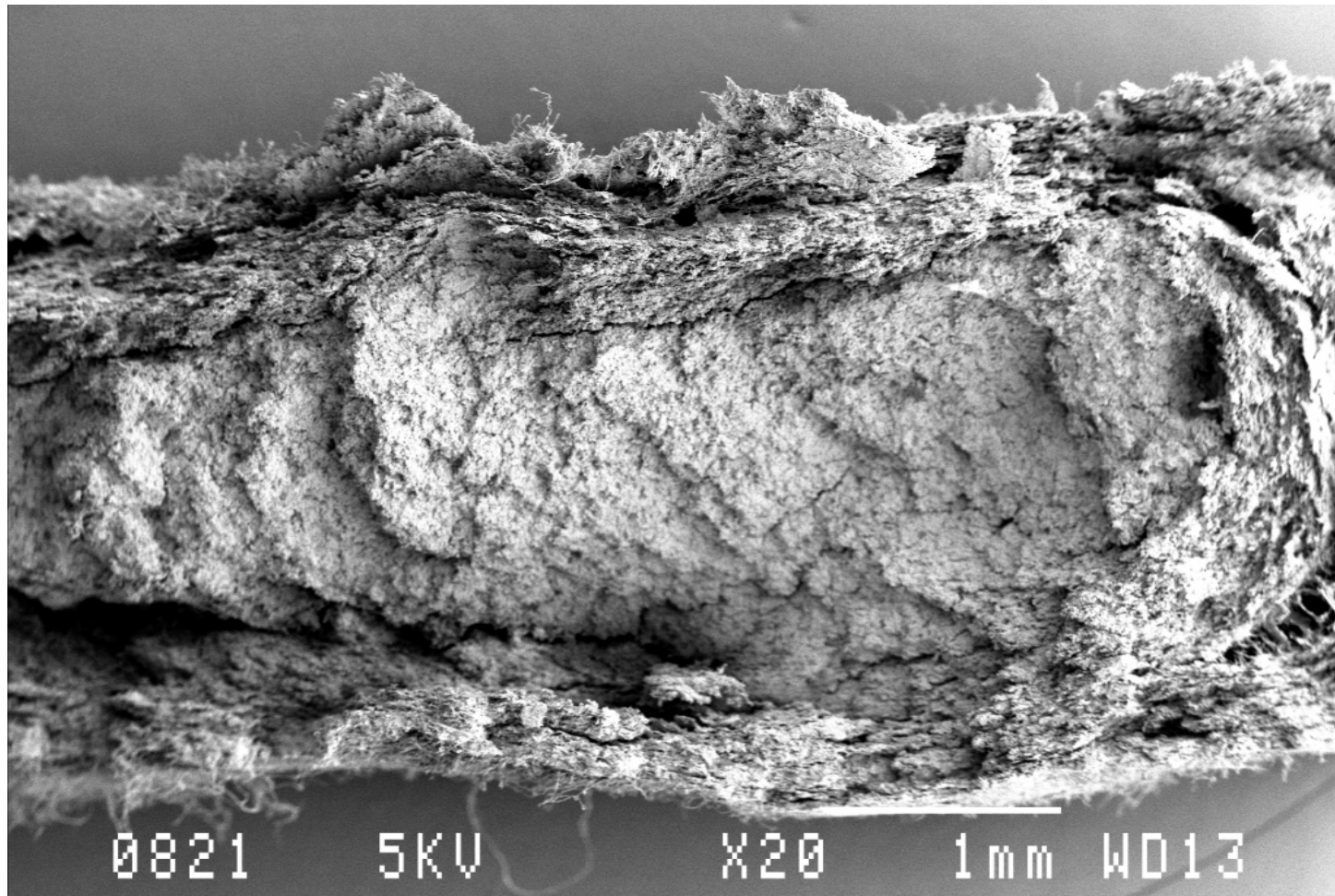


Figure F8: Aerobic and anaerobic layers of biodegradation in TPS PVB. Photo taken at day 45 of the composting at x20 magnification.

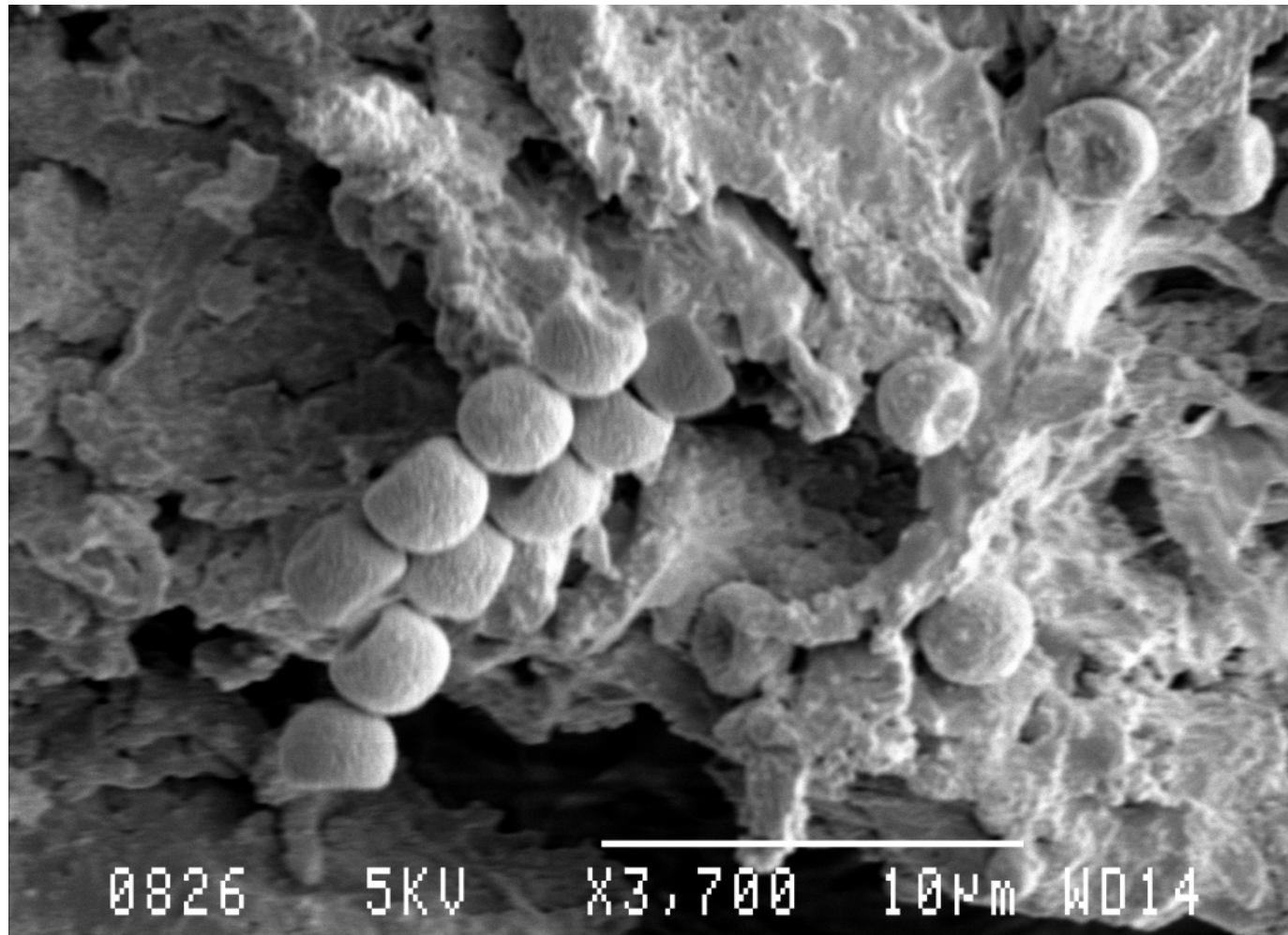


Figure F9: Hife in TPS PVB. Photo taken at day 45 of the composting, outside composting layer and magnification of

x3 700

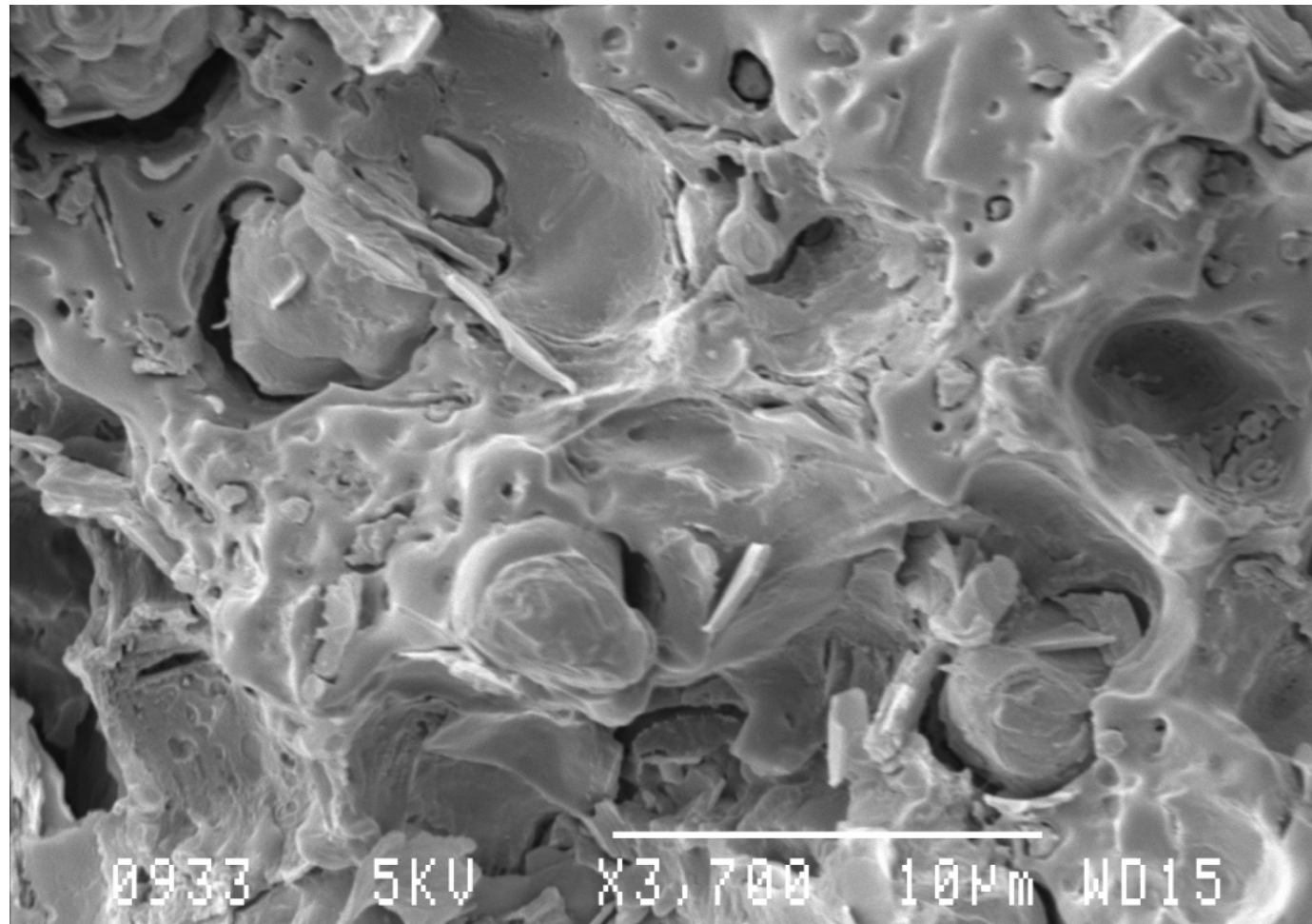


Figure F10: U20/Hi20 at day 60 of composting. Starch granules still visible under the slime mucus. Photo taken from the inside composting layer at magnification x3 700.

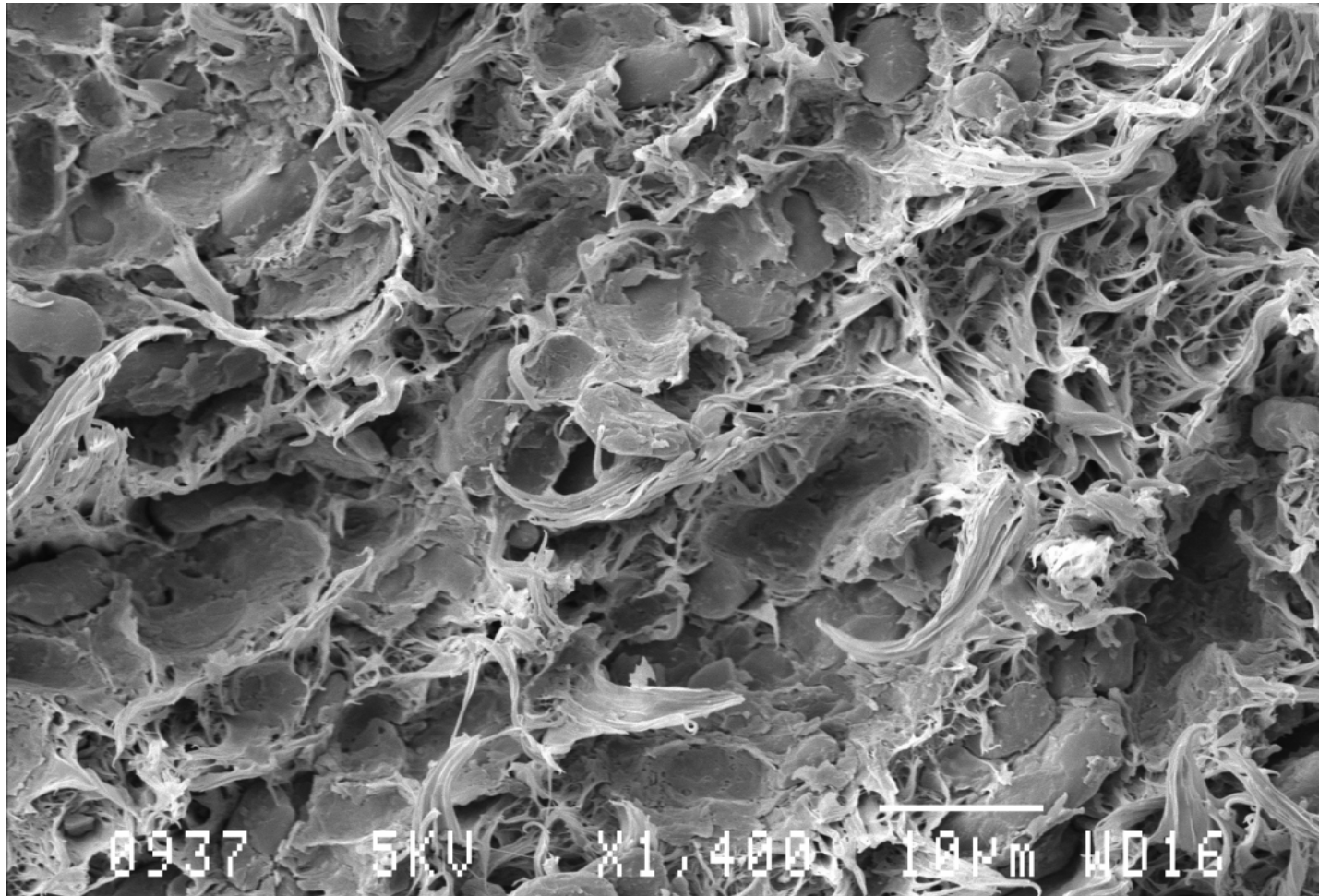


Figure F11: Complete degradation in the outer aerobic layer in U20/Hi20 composition. Photo taken from the outside decomposing layer at day 60 of the test and magnification x1 400.

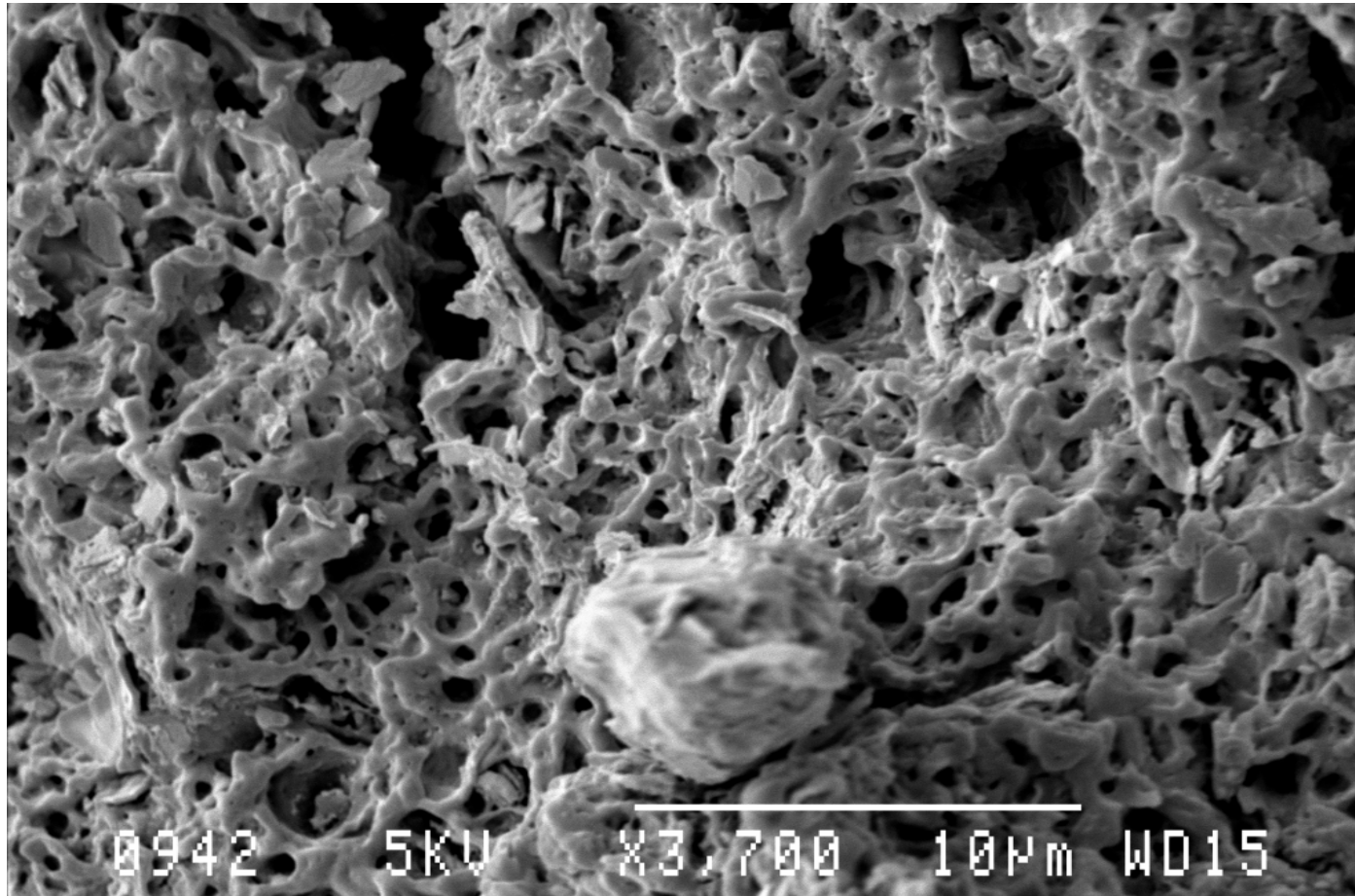


Figure F12: Complete degradation in the inner layer of U40 composition, compostability day 60 and magnification x3 700.

Figure 1