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

By

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ABSTRACT

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

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

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

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

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

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

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

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

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DEFINITIONS

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

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

LIST OF ABBREVIATIONS

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