Materials Science and Engineering A 532 (2012) 178–189

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering A

journal homepage: www.elsevier.com/locate/msea

Characterization of water-free thermoplastic starch blends for manufacturing processes

P. Lescher, K. Jayaraman, D. Bhattacharyya

Centre for Advanced Composite Materials, Department of Mechanical Engineering, The University of Auckland, Private Bag 92019, Auckland, New Zealand

ARTICLE INFO

Article history:
Received 18 August 2011
Received in revised form 17 October 2011
Accepted 17 October 2011
Available online 26 October 2011

Keywords:
Mechanical characterization
Polymers
Aging

ABSTRACT

As part of an investigation into the use of cheap water-free thermoplastic starch (TPS) as a filler in rotomoulding applications, TPS/PE (polyethylene) blends were manufactured and tested as extruded strands, injection-moulded samples and rotomoulded samples. The effects of starch type, plasticizer type and amount as well as compatibilization on mechanical properties have been investigated. Ultimate tensile strength was found to be consistent across different manufacturing methods and after aging; tensile modulus was more dependent on manufacturing method and TPS formulation. High-amylose starches improved mechanical properties at low plasticizer contents but hydroxypropylation did not. Small amounts of compatibilizers improved strength and stiffness; larger quantities of octenyl-succinic anhydride modified starch improved consistency while preserving strength, stiffness and ductility. The highest blend strengths, as well as lowered ductility, were found in strand tests where TPS/PE modulus approached that of the PE.

1. Introduction

Starch is an abundant, cheap biodegradable material, which has been used as a filler in polymers and a thermoplastic in its own right [1,2]. Polymer blends based on thermoplastic starch (TPS) have been used to lower costs, enhance degradability and alter the properties of other materials. TPS is typically plasticized by water and glycerol. Plasticizer contents are often high, partly to improve processing properties. Work by Liu et al. [3] demonstrated improved processability with a drop in the melting transition from 197 °C to 136 °C as glycerol content was increased from 23% to 33.3%. While the onset of degradation at high temperatures was also lowered, the overall processing temperature range was wider. They also demonstrated that within specified shear rates, the glycerol content could be used to tune TPS viscosity to approximate that of linear low-density polyethylene (LLDPE).

Furthermore, while processes, such as extrusion, result in depolymerization due to heat and shear, Forssell et al. [4] have shown that higher glycerol contents can mitigate the drop in molecular weight due to melt-blending. This was shown to be due to glycerol rather than total plasticizer content; lower glycerol levels resulted in more depolymerization despite higher water contents.

The ubiquity of polyethylene (PE) and its similar viscosity to TPS make it an ideal polymer with which to examine the properties of TPS in a blend. However, TPS and PE can be viewed as not particularly compatible given the hydrophilic nature of TPS and the hydrophobicity of PE. One study [5] used the copolymer polyethylene-g-maleic anhydride (PE-g-MA) to couple the two materials, but recent work by Rodriguez-Gonzales et al. [6,7] has demonstrated excellent blends of glycerol-plasticized starch and PE, without the use of a modified starch or compatibilizers, using a single multiple-stage extrusion, venting water used in the initial mixture before adding PE. Interestingly, the dynamic shear viscosity was shown to drop 20% between 36% and 40% glycerol. The authors suggested a transition between the dominance of a crystalline phase and that of a soft glycerol-rich amorphous region consistent with percolation theory. This implies a distinct upper limit for glycerol content beyond which TPS will become substantially softer and weaker.

Glycerol is usually used in conjunction with water; the work by Rodriguez et al. is an exception in that while the initial ingredients include water, the blends are ostensibly water-free due to removal at the vacuum port. Glycerol-plasticized starch without a significant water content is not a common product due to the fact that water will typically be absorbed even after manufacture. Nonetheless other authors have reported blends in which moisture has apparently been avoided during manufacture [8].

TPS has been shown to retrograde at a faster rate over time due to increased plasticizer content lowering the T_g and raising polymer mobility [9]. Van Soest demonstrated the glycerol and water contents to have an effect on crystallinity both in fresh samples and during aging [10]. Huang et al. [11] demonstrated that while

E-mail address: ples001@aucklanduni.ac.nz (P. Lescher).

0921-5093/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.msea.2011.10.079

glycerol-plasticized starch shows an increase of V_h crystallinity over a 90-day period after manufacture, when ethanolamine is substituted for glycerol no such recrystallization occurs. This behaviour may be useful in producing more stable TPS blends.

The nature of starch itself makes it open to direct modification instead of blending. High-amylose starch can be obtained from hybrid corn stocks, and is available in grades of up to 90% amylose. It crystallizes rapidly after extrusion and needs far less plasticizer—it has in fact been shown that plasticizer has less of an effect on high-amylose starch [12]. It has much higher mechanical properties than most common starches which have amylose contents of around 20–25%, although it is more expensive. The amylose molecule itself may also be modified as in the case of hydroxypropylated starch, which may be created by extrusion and is commercially available. It is commonly used as a higher-performance alternative to water-soluble starch packing peanuts as it is both water resistant and has a higher expansion, closer to that of expanded polystyrene (EPS). National Starch produces such packaging pellets branded as Eco-foam. High-amylose hydroxypropylated starches and other highly modified starches may be extruded without any plasticizers at all and have been referred to as "thermoplastically processable starch" [13].

This work centres around the use of variations of a TPS/PE blend which has been demonstrated to be suitable for rotational moulding and other consumer plastic manufacturing methods [14]. The novelty of this material is in the fact that unlike TPS-based materials created commercially and reported about in the literature, it is effectively water-free during manufacture. It is, therefore, an interesting material to study in terms of its blending compatibility with other polymers, as well as mechanical and functional properties. It has the potential to be used for different manufacturing processes and reduce the cost of rotational moulding, a process dominated by PE. TPS blends with hydrophobic polymers are already used commercially as oxygen barriers [15] and are easily foamed without water [16]; blends incorporating water-free TPS with hydrophobic polymers may be particularly useful in multilayered materials, where foamed cores and gas barrier layers are protected from moisture.

2. Methods

2.1. Materials, production and testing

Avon maize starch (≈25% amylose), Gelose 50 (>50% amylose), Gelose 22 (a hydroxypropylated starch similar to Gelose 50) and octenyl succinate anhydride (OSA) modified starch were purchased from Penford NZ. High-purity (≥99%) glycerol and ethanolamine were obtained from Scientific Supplies and Sigma–Aldrich®, respectively. Cotene™ 9042 linear medium density polyethylene (PE) from ICO Polymers, Inc. was chosen as a suitable rotomouldable base polymer throughout this work. Fusabond™ EM-B226D from DuPont, an anhydride-modified LLDPE, was chosen as a compatibilizer for PE.

Starch was first dried in a vacuum oven at 100 °C for at least 12 h before addition of glycerol and ethanolamine. Mixtures were left to settle in the oven for a further 12 h at a reduced temperature of 70 °C before hand mixing with PE and Fusabond. Melt-blending was carried out in a starve-fed co-rotating twin-screw extruder (Brabender DSE20) with a screw diameter of 20 mm and L/D ratio of 40. The screw configuration incorporated both transport and mixing zones. Material was drawn through a 3 mm circular die at 4–7 m/min while air-cooled by forced convection. Blends were collected in strand form for direct testing, or pelletized for further processing. Injection moulded 12.7 mm × 3.1 mm cross-section type 1 "dogbone" samples conforming to ASTM D638 were created in a Boy 50 A injection moulder. A Retsch SM100 centrifugal mill was used to powder blended pellets before rotomoulding in a custom-made "rock and roll" rotomoulding oven. Powder was conditioned overnight at 70 °C under vacuum, before being rotomoulded in a vented aluminium rectangular mould with a teflon-coated internal cavity of 210 mm × 220 mm × 190 mm. Oven temperature was kept at 220 °C with a thermocouple and PID controller. Air temperature inside the mould cavity was monitored by a second thermocouple; a maximum cavity temperature of 150 °C was reached before fan-forced air cooling. A shot size of 850 g was used in all cases, giving an average wall thickness of 3.5 mm in the resulting specimens, which were cut into 170 mm × 12.7 mm strips for tensile tests.

Tensile properties were evaluated in an Instron 5567 Universal testing machine. The cross-sectional area of strands was calculated by taking two perpendicular diameter readings and assuming them to be the major and minor axes of an ellipse. Two areas 50 mm apart were calculated and averaged for each strand area measurement. All other samples were measured as specified in ASTM D638 for dogbone samples. Tensile modulus was calculated as a chord between 0.05% and 0.25% strain, following an in-house convention based on the ISO 527–1:1993(E) standard. Extruded strands were held between drum grips to avoid pinching, while conventional grips were used for other samples. Marks on the samples were tracked with a video extensometer to determine strain in a 50 mm gauge length while samples were drawn at a rate of 5 mm/min. Ultimate tensile strength (UTS) and elongation behaviour were then obtained at 500 mm/min, and the test concluded at 500 mm extension if the sample had not yet broken.

2.2. Experimental design

An 8-run, 2-level full-factorial Taguchi L_8 experiment was conducted to investigate effects due to the factors shown in Table 1, as well as interactions between these effects, on UTS and modulus. The experiments were conducted with extruded strands, injection moulded and rotomoulded samples. The TPS/PE ratio was fixed at 20:80 by mass, while the extruder and die temperatures were set at 160 °C, and mass flow rate was set at 10 g/min. Screw speed was varied to keep torque below the 60 Nm limit of the extruder. Samples were tested within 24 h of manufacture. Extruded and injection moulded samples were stored and re-tested after 80 days; rotomoulded samples were re-tested after 60 days.

While the factorial investigation was intended to give a broad picture of the material behaviour across a number of manufacturing methods and blends, a more detailed series of tests were also carried out to investigate incremental changes in plasticizer content, the effect of compatibilizers and the ductility of blends. Modulus and UTS tests were conducted with 20:80 maize TPS35/PE (TPS with 35% glycerol content) strands with increasing OSA starch or Fusabond amounts substituted in place of maize or PE respectively, to determine the effect of compatibilization. Ductility was investigated in terms of elongation at break in UTS testing. In order to obtain more detailed information on the effect of plasticizer, the same strand properties were also tested with 30:70 TPS/PE and glycerol contents from 15% to 40% in 5% increments with maize starch, Gelose 50 and Gelose 22.

Table 1
Factors used as variables in the manufacture of extruded strands.

Factor	Level 1	Level 2
Starch type (A)	Maize starch	Gelose 50
Plasticizer type (B)	Glycerol	50:50 glycerol/ethanolamine
Plasticizer content in TPS phase (C)	15%	35%