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Comparison of Sorbitol and Glycerol as Plasticizers for Thermoplastic Starch in TPS/PLA blends

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COMPOUNDING AND PROPERTIES OF TPS/POLYMER BLENDS

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Abstract

This paper examines the structure development and properties of thermoplastic starch blended with high density polyethylene, polypropylene, polystyrene, poly(lactic acid) and polycaprolactone. The TPS gelatinization and mixing with the second polymer was carried out on a twin-screw extruder. Addition of maleated polymers was evaluated as a means to compatibilized the blends. Starch gelatinization was assessed using X-ray diffraction. Blend morphologies were probed by scanning electron microscopy and mechanical properties were evaluated from tensile testing. The use of maleated polymers was shown to be very effective in the compatibilization of TPS/polymer blends.

Introduction

Thermoplastic starch is produced by mixing native starch with a plasticizer at a temperature above the starch gelatinization temperature, typically in the 70-90°C range. This operation weakens the hydrogen-bonds present in the native starch leading to a fully amorphous free-flowing material. The resulting material is known as plasticized starch, destructured starch or thermoplastic starch (TPS). The properties and rheology of thermoplastic starch have been thoroughly investigated [1-4]. As such, the TPS is not a suitable material for most common uses. It is very hygroscopic and its properties and dimensional stability are strongly affected by the humidity level since water is a plasticizer for TPS. Also in presence of humidity, the amorphous TPS tends to reform its hydrogen-bonds leading to recrystallization (also called retrogradation) and in turn to embrittlement of the material. This strong property dependence on plasticizer content can become an advantage however when the TPS is blended with another hydrophobic polymer. In this case, the hydrophobic polymer can protect the TPS from direct water contact and moisture uptake while the plasticizer level in the TPS can be used to tune the mechanical properties of the TPS. Therefore, the vast majority of work involving the use of starch as a material has focused on blending of TPS and other synthetic polymers [5-7]. The synthetic material can be biodegradable to produce a fully compostable material or can be non-biodegradable to produce materials for longer-term applications. Examples of biodegradable blends include blends of TPS with polycaprolactone or polybutylene succinate which are two petrochemical based polymers. With the recent commercial introduction of PLA, there has also been a high interest for PLA/TPS blends and these have been investigated in terms of their compatibility [8] and of their processing into injection molded product , biaxially oriented films [9] and low-density foams [10].

The compounding process used for the preparation of TPS/polymer blends is relatively complex. It must nominally enable the precise metering of starch and plasticizers, the starch gelatinization and the mixing of the TPS with the second polymer phase to obtain finely dispersed or finely segregated blend morphology. Additionally, more elaborate functions may be performed. For example, venting or devolatilization may be used to control volatiles levels. Interface modification through in situ interfacial reaction may be used to compatibilize the blend or to modify the starch interface. Surprisingly, very little scientific publications have focused on the structure development along this compounding process and little guidance can be found as to what could be the best practices in terms of TPS/polymer blend compounding technology.

This paper examines the structure development of different TPS/polymer blends obtained by twin-screw compounding. The investigations covered compatibilized and uncompatibilized blends of TPS with high density polyethylene (PE), polypropylene (PP), polystyrene (PS), polylactic acid (PLA) and polycaprolactone (PCL). The TPS gelatinization was accessed using x-ray diffraction (XRD), the blend morphology development was examined using scanning electron microscopy (SEM). In addition, the moisture content and mechanical properties of the TPS prior to mixing with the second polymer phase were determined and the properties of the resulting blends were examined.

Experimental

Materials. Wheat starch was used as the sole starch source. The starch was an industrial purpose starch grade, Supergel 1201, supplied by ADM. The grade names and suppliers of PE, PP, PS, PCL and PLA are summarized in Table 1. The blend composition was set to 25%TPS for all TPS/polymer blends.

based blends, the modulus and strength of the blends was similar to that of the PE and PP matrices. The elongation was severely decreased in the non-compatibilized TPS/PE blend and for both TPS/PP blends. For the compatibilized PE based blend, the samples were able to extend up to the maximum extension of the tensile testing equipment (i.e. 800%). PS and PLA are more rigid matrices. The addition of the TPS therefore decreased the modulus and strength in a more significant way but left nearly unchanged the already low elongation at break of the matrices. The TPS and PCL are known to be more compatible without the use of an interfacial modifier. The tensile modulus and strength were decreased with addition of the TPS phase but the elongation at break remained in excess of 800%.

Table 4. Tensile properties of blends

	With MAh copolymer	Modulus (GPa)	Tensile strength (MPa)	Elong. at break (%)
PE		1.12	17.9	>800
TPS/PE	No	1.05	15.8	233
	Yes	0.935	16.0	>800
PP		1.00	18.8	700
TPS/PP	No	0.914	16.4	12
	Yes	0.989	18.0	44
PS		3.28	37.0	2.0
TPS/PS	No	2.97	31.0	2.1
	Yes	2.87	31.9	2.0
PLA		3.68	69.2	6.0
TPS/PLA	No	3.33	46.6	4.0
	Yes	2.96	45.8	6.8
PCL		0.43	25	>800
TPS/PCL	No	0.259	11.0	>800

Conclusions

This paper has investigated the structure development during the TPS/polymer compounding process and properties of various TPS/Polymer blends. Complete gelatinization was obtained at the end of the first mixing zone of the twin-screw extrusion process. Coarse blend morphologies were developed in unmodified blends. The partial substitution (10%) of the matrix materials by maleated analogs produced a dramatic reduction in TPS dispersed phase size. Tensile strength and modulus of rigid polymers such as PLA and PS are reduced by the addition of the TPS as expected from mixing rules. For lower modulus polymers, the drop in tensile strength and modulus was not as significant. The elongation at break was also maintained to the same level as blend matrices in the case of the compatibilized TPS/PE and in TPS/PCL.

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