



High performance polyethylene/thermoplastic starch blends through controlled emulsification phenomena

Claire Cerclé^a, Pierre Sarazin^b, Basil D. Favis^{a,*}

^a CREPEC, Department of Chemical Engineering, Ecole Polytechnique de Montréal, 2900 Edouard Montpetit, P.O. 6079, Station Centre-Ville, Montréal, Qc, H3C 3A7, Canada

^b Cerestech Inc., Pavillon J.-A. Bombardier, 5155 Ave. Decelles, Montréal, Qc, H3T 2B1, Canada

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ABSTRACT

The emulsification efficacies of a range of compatibilizers for polyethylene/thermoplastic starch blends have been studied and a detailed morphological and mechanical analysis has been conducted. It is shown that polyethylene–maleic anhydride terpolymers containing elastomeric segments provided excellent emulsification of PE/TPS blends with a fine morphology (volume diameter of 1.4 μm ; number average diameter of 600 nm). The blends compatibilized with these copolymers exhibit a very high elongation at break of about 800%, the highest value ever reported for PE/TPS systems. Also, significant improvement in notched impact strength performance at interfacial saturation was found for these systems leading to specimens with an equivalent performance to pure polyethylene. An excellent correlation was found between the critical concentration for interfacial saturation and the mechanical properties, indicating the key role of morphology.

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1. Introduction

Starch is a natural carbohydrate storage material accumulated by green plants in granular form and is composed of amylose (linear molecules) and amylopectin (branched molecules). It is a renewable, inexpensive natural polymer that can be blended with synthetic polymers in order to decrease their relative amount and to lower the cost of the final product. Griffith was one of the pioneers who prepared a starch-filled polyethylene (PE) composite (Griffin, 1977). However, the addition of starch to PE resulted in a drastic decrease of its tensile strength and elongation at break (Evangelista, Nikolov, Sung, Jane, & Gelina, 1991; Willett, 1994).

The crystalline structure of starch can be disrupted by a process called gelatinization (French, 1984). In that process, starch is first mixed with water and is subsequently stirred and heated, resulting in the disruption of the crystalline structure due to the formation of hydrogen bonds between water molecules and the free hydroxyl groups of starch. In this state, starch can flow. Otey and co-workers (Otey, Westhoff, & Doane, 1980, 1987) produced gelatinized starch/ethylene acrylic acid (EAA) cast films that showed good transparency, flexibility and mechanical properties. Gelatinized starch can then be subsequently plasticized by the addition of a suitable plasticizer such as glycerol. This material, known as

thermoplastic starch (TPS), can flow at elevated temperatures and shows good ductility, which makes it convenient for melt processing.

TPS can be melt-blended with polyolefins (Bikiaris et al., 1998; Favis, Rodriguez-Gonzalez, & Ramsay, 2003; Rodriguez-Gonzalez, Ramsay, & Favis, 2003; Taguet, Huneault, & Favis, 2009) or with biodegradable polymers (Averous & Fringant, 2001; Averous, Fauconnier, Moro, & Fringant, 2000; Ma, Hristova-Bogaerds, Schmit, Goossens, & Lemstra, 2012; Teixeira et al., 2012; Sarazin, Li, Orts, & Favis, 2008; Walia, Lawton, & Shogren, 2002). In a previous work from this laboratory, (Favis et al., 2003; Rodriguez-Gonzalez et al., 2003) developed a one-step melt extrusion process for LDPE/TPS blends that permitted an effective control over the morphology as well as the continuity level of the TPS phase, resulting in good mechanical properties. The authors obtained 96% of the elongation at break and 100% of the modulus of LDPE in a 71/29 LDPE/TPS blend. It should be underlined that a high level of plasticizer is required in the TPS in order for it to be sufficiently fluid to undergo the phase deformation/disintegration phenomena required for morphology deformation. These authors also examined the effects of coalescence and particle deformation during melt drawing of these blends systems.

Binary blends of TPS and polyolefins have a relatively high interfacial tension due to the high incompatibility of the non-polar polyolefin and the highly polar TPS (Chandra & Rustgi, 1997; Willett, 1994). It is possible to improve their compatibility through the addition of a suitable interfacial modifier (Bikiaris, Prinós, &

* Corresponding author. Tel.: +1 514 340 4711x4527; fax: +1 514 340 4159.
E-mail address: basil.favis@polymtl.ca (B.D. Favis).

Table 1
Description and properties of the materials used for the blends.

Material	Density (g/cm ³)	MFI at 190 °C (g/10 min)	Wt.% of R _x	Wt.% of MA	M _n ; M _w (g/mol)
HDPE (Sclair® 2710)	0.951	17	–	–	–
Wheat starch (Supergell® 1203-C, ADM)	1.4	–	–	–	M _v ~ 70,000 ^c
Glycerol (Labmat)	1.26	–	–	–	92.09; –
PP-g-MA ^a	–	–	–	~3	~32,000; 77,000
PE-g-MA ^a	0.95	12	–	3.9 ^d	31,200; 112,500
PE-R ₁ -MA ^b	0.94	6	High	~3	12,700; 88,000
PE-R ₂ -MA ^b	0.94	3	Medium	~3	~16,800; 92,000
PE-R ₃ -MA ^b	0.94	9	Low	~4	11,400; 73,800

^a Polypropylene and polyethylene grafted with maleic anhydride.

^b Polyethylene-R_x-MA where the R_x groups are elastomeric segments containing is a –OCH₃, –OC₂H₅ and –OC₄H₉ respectively. The maleic anhydride, as the R_x groups, is not grafted but randomly distributed on the polymer chain.

^c Measured by intrinsic viscosity (M_v: average viscosity molecular weight).

^d Measured by elementary analysis.

Panayiotou, 1997; Bikiaris et al., 1998; Giriya & Sailaja, 2006; Sailaja & Chanda, 2000; Sailaja, Reddy, & Chanda, 2001). One of the most common modifiers used for the compatibilization of TPS/PE blends is polyethylene grafted with maleic anhydride (PE-g-MA) (Bikiaris et al., 1997, 1998; Sailaja & Chanda, 2000; Wang, Yu, & Yu, 2005a, 2005b). The esterification reaction between the maleic anhydride groups of the PE-g-MA and the hydroxyl groups of the starch results in the in situ formation of a grafted copolymer that improves interfacial interactions, leads to a decrease of the dispersed phase size and improves the mechanical properties (Bayram, Yilmazer, Xanthos, & Patel, 2002; Bikiaris & Panayiotou, 1998; Ramkumar, Bhattacharya, & Vaidya, 1997; Wang et al., 2005a, 2005b).

In a previous work from this laboratory (Taguet et al., 2009), it has been demonstrated that glycerol-rich domains in the TPS dispersed phase tend to migrate to the PE/TPS interface. This results in a very thin glycerol-rich layer at the interface. The optimum mechanical properties were obtained when 36% of glycerol was used for the blends. A PE-g-MA interfacial modifier was used to compatibilize the PE/TPS interface and it was suggested that a portion of the copolymer was not finding its way to the interface.

The main objective of this work is to examine the efficacy of various polyethylene-based copolymers on their ability to emulsify PE/TPS blends. The use of copolymers here is motivated by the desire to develop high performance bioplastics that can be used in the semi-durable and durable application fields. Detailed characterization of the emulsification phenomena will be determined through the use of an emulsification curve which tracks the size of the dispersed phase evolution with the wt.% of copolymer. The copolymer efficacy will be related to the chemical composition, molecular weight, interfacial saturation and areal density of the copolymer at the interface. Finally, the relationship between these various parameters and the mechanical properties will be studied in detail.

2. Experimental part

2.1. Material

The high-density polyethylene (HDPE) was supplied by Nova Chemicals (Sclair® HDPE 2710, MFI=17). The native wheat starch (20–28% amylose, 72–80% amylopectin (Averous, 2004; Tester & Morrison, 1990), Supergell 1203-C) and the pure glycerol (99.5% purity with 0.5% water) were obtained from ADM and Labmat respectively. Five different interfacial modifiers with maleic anhydride (MA) were tested: polypropylene grafted maleic anhydride (PP-g-MA); polyethylene grafted maleic anhydride (PE-g-MA); and three different random ethylene-R_x-maleic anhydride interfacial modifiers. R_x is an elastomeric segment containing –OR groups. These latest compatibilizers (PE-R_x-MA) used in this study are denoted as PE-R₁-MA, PE-R₂-MA and PE-R₃-MA where R₁ refers

to an elastomeric segment containing –OCH₃ groups, R₂ to –OC₂H₅ groups and R₃ to –OC₄H₉ groups respectively. Note that the maleic anhydride and the R_x elastomeric segments are not grafted but are randomly distributed in the polymer chain. The characteristics of all the materials are given in Table 1. The compatibilizers used in this study were not made in-house, but are proprietary materials supplied by industry.

2.2. Blend preparation

Starch granules were gelatinized, plasticized with glycerol and water and blended with HDPE and compatibilizer in a one-step extrusion process. Blends were prepared containing 20 wt.% of TPS and 80 wt.% of HDPE. The TPS contains 36% of glycerol. The compatibilizer was added with the HDPE, at various rates. All compatibilizer concentrations are based on the TPS content.

The processing of the polyethylene/thermoplastic starch blends was based on a process developed previously in this laboratory (Favis et al., 2003). More detailed information related to the process is given in those articles. The extrusion system was composed of a single-screw extruder (SSE) connected midway to a co-rotating twin-screw extruder (TSE). A starch/glycerol/water suspension was fed in the first zone of the TSE. Native starch was gelatinized and plasticized and volatiles were extracted in the first part of the TSE. Molten HDPE and copolymer (T = 160 °C) were fed from the SSE to midway on the TSE. TPS, HDPE and copolymer were then mixed in the latter part of the TSE. The TSE screw speed was 150 rpm for all blends. A three-hole strand die (diameter 3 mm) was used and strands were water cooled, followed by air cooling and then pelletized.

Note that the TPS with 36% of glycerol is prepared from a suspension containing 28.1 wt.% glycerol. The 36% in the TPS corresponds to the weight of glycerol divided by the weight of glycerol and starch (including ambient water in the as-received starch, but not including any added excess water). After plasticization of the starch, water was removed using a venting process. Under such conditions, virtually all of the water was removed (including native water within the as-received starch).

2.3. Scanning electron microscopy and image analysis

Prior to the blends being cut into 3 mm pellets, some strand were taken out and cut into 1 cm long cylinders. Samples were then cryogenically microtomed at –150 °C with a glass knife perpendicular to the extrusion direction using a Leica RM 2165 microtome equipped with a Leica LN 21 cryochamber. The TPS phase was subsequently extracted from the samples using 6 N HCl for 3 h at room temperature. The samples were subsequently washed with water, dried under air overnight and coated with a gold–palladium alloy by plasma sputtering for 45 s. The SEM observations were carried

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