



## Study on ternary low density polyethylene/linear low density polyethylene/thermoplastic starch blend films



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### ABSTRACT

In this work, low-density polyethylene/linear low-density polyethylene/thermoplastic starch (LDPE/LLDPE/TPS) films are prepared with the aim of obtaining environmentally friendly materials containing high TPS content with required packaging properties. Blending of LDPE/LLDPE (70/30 wt/wt) with 5–20 wt% of TPS and 3 wt% of PE-grafted maleic anhydride (PE-g-MA) is performed in a twin-screw extruder, followed by the blowing process. Differential scanning calorimetric results indicate starch has more pronounced effect on crystallization of LLDPE than LDPE. Scanning electron micrograph shows a fairly good dispersion of TPS in PE matrices. Fourier transfer infrared spectra confirm compatibility between polymers using PE-g-MA as the compatibilizer. Storage modulus, loss modulus and complex viscosity increase with incorporation of starch. Tensile strength and elongation-at-break decrease from 18 to 10.5 MPa and 340 to 200%, respectively when TPS increases from 5 to 20%. However, the required mechanical properties for packaging applications are attained when 15 wt% starch is added, as specified in ASTM D4635. Finally 12% increase in water uptake is achieved with inclusion of 15 wt% starch.

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### 1. Introduction

Blends of low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) have gained many attentions in film packaging applications. LDPE exhibits good processability and high melt strength due to its long chain branching. Conversely, LLDPE is well known for superior mechanical properties e.g. higher tensile strength, elongation at break and impact strength. Therefore, LDPE/LLDPE blends would provide processability and mechanical properties, simultaneously. Another advantage of LDPE/LLDPE blending is using the conventional LDPE film blowing apparatus without modification (Hemati & Garmabi, 2011; Lu & Sue, 2002; Yilmazer, 1991).

Today, there has been an increased interest in producing environmentally friendly materials by blending polyethylene with natural polymers. Because, the waste disposal of these films owing to their non-biodegradability causes a growing problem of environmental pollution (Kahar, Ismail, & Othman, 2012; Prachayawarakorn, Sangnitdej, & Boonpasith, 2010). Starch is among the most commonly used biofiller in polyethylene because of its abundant availability and low cost (Ning, Jiugao, Xiaofei,

& Ying, 2007; Pushpadass, Bhandari, & Hanna, 2010). It is well established that starch-filled PE materials because of their incompatibility present poor mechanical properties such as tensile strength and elongation at break (Shujun, Jiugao, & Jinglin, 2006). To overcome this drawback and to achieve the expected properties, many attempts have been conducted on modifying either starch or PE (Kim, 2003; Yoo et al., 2002). In addition, using a plasticizer to provide a good dispersion of starch in the polymer matrix and an increase in susceptibility to biodegradation has been approved (Garg & Jana, 2007; Wang, Liu, & Sun, 2004). Glycerol owing to its low cost and availability is the most widely used plasticizer to prepare a material known as thermoplastic starch (TPS) (Mohammadi Nafchi, Moradpour, Saeidi, & Alias, 2013).

Data in the literature indicate that plasticizing agents due to their limited interactions partially improve dispersion of starch in PE and decrease interfacial tension between them (Liu, Wang, & Sun, 2003). It has been found that using some materials as the compatibilizer would be more effective approach. Polyethylene-grafted maleic anhydride (PE-g-MA) is one of the most common compatibilizers used to promote interfacial adhesion, reduce the size of dispersed phase and also improve the mechanical properties to some extent. In such circumstances, addition of higher amount of TPS to PE would be probable (Taguet, Huneault, & Favis, 2009; Wang, Yu, & Yu, 2005).

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Blends of starch with LDPE or LLDPE have been extensively reported in the literature and they are still an interesting subject to be further investigated (Cerclé, Sarazin, & Favis, 2013; Oromiehie, Iari, & Rabiee, 2013; Taghizadeh, Sarazin, & Favis, 2013). Some efforts have been made to prepare PE/starch materials with required properties, being alternative of commodity PE plastics for packaging uses. It has been known that reduction in mechanical properties of PE is inevitable when starch content increases. However, these materials with optimized level of starch can be used in packaging applications (Gupta & Sharma, 2010; Jagannath, Nadanasabapathi, & Bawa, 2006; Rodriguez-Gonzalez, Ramsay, & Favis, 2003; Sabetzadeh, Bagheri, & Masoomi, 2012).

In our previous study (Sabetzadeh et al., 2012), it has been demonstrated that LDPE/TPS blends would satisfy the requirements of disposal products for packaging uses. The expected mechanical properties are obtained when 25 wt% of TPS is added. In the present study, an attempt is made to produce environmentally friendly materials having potential abilities in film applications. To address this issue, LDPE/LLDPE (70/30 wt/wt) blend is melt compounded with various amounts of TPS (5, 10, 15 and 20 wt%) in a twin screw extruder and then blown to obtain thin films. Glycerol and PE-g-MA are used in the polymer matrices as the plasticizer and compatibilizer, respectively. Determination of high filling of starch into LDPE/LLDPE blend without affecting the required mechanical properties of PE packaging films is our main purpose. To provide more investigation, thermal and dynamic properties along with water absorption which is related to biodegradability of the films are elucidated as a function of TPS loading.

## 2. Experimental

### 2.1. Materials

Two commercial film grades of polyethylene were used: (1) LDPE with a melt flow index (MFI) of 0.75 g/10 min and a density of 0.921 g/cm<sup>3</sup>; (2) LLDPE with MFI of 0.9 g/10 min (190 °C, 2.16 kg) and a density of 0.920 g/cm<sup>3</sup>, which supplied by Petrochemical Commercial Company, Iran. The native corn starch (30 wt% amylose) was obtained from Glucosan Company, Iran. Glycerol (99.5% purity) as a plasticizer for starch was purchased from Hansa Group AG, Germany. Polyethylene grafted maleic anhydride (PE-g-MA) was provided by Pluss Polymers Co, Ltd. (India) and used as a compatibilizer.

### 2.2. Melt blending and film blowing

Prior to blending, all ingredients were dried in a vacuum oven at 80 °C for 24 h. Thermoplastic starch (TPS) was prepared by melt mixing the homogenous compound of native starch and 35 wt% glycerol in a Haake internal mixer (with a volumetric chamber capacity of 300 cm<sup>3</sup>) at 140 °C with rotor speed of 60 rpm for 8 min.

The prepared TPS was melt blended with LDPE/LLDPE (70/30 wt/wt) mixture and 3 wt% PE-g-MA (based on the blend weight) in a twin screw extruder (model ZSK25, Germany). The extruder had screw diameter (*d*) of 25 mm and the length to diameter ratio (*L/D*) was 40. The temperature profile along the six heating zones of the extruder barrel was 140–180 °C (from feed zone to die) and the screw speed was set at 150 rpm. TPS loadings were ranged from 0, 5, 10, 15 and 20 wt%. The prepared blends were emerged in the form of continuous strands through the die. The strands were cooled using water trough and pelletized. The pellets were then blown into 45 μm thick films using Dr Collin single screw extruder (model E45M) with *L/D* ratio of 25, containing eight zones. A temperature profile of 145–155 °C was maintained during the process

**Table 1**

The sample codes and formulations of all the prepared LDPE/LLDPE/TPS films.

Sample code	LDPE/LLDPE (wt/wt)	TPS (wt%)	PE-g-MA (wt%)
LD/LL/TS0 <sup>a</sup>	70/30	0	3
LD/LL/TS5	70/30	5	3
LD/LL/TS10	70/30	10	3
LD/LL/TS15	70/30	15	3
LD/LL/TS20	70/30	20	3

<sup>a</sup> Reference film sample.

and the screw speed was set at 70 rpm. The blend formulations and sample codes are summarized in Table 1.

### 2.3. Characterization

Thermal behavior of LDPE/LLDPE/TPS films was characterized by differential scanning calorimetry (Mettler Toledo DSC 822e Thermal Analyzer, Switzerland) in nitrogen atmosphere under a flow rate of 50 mL/min. A sample weight of 7 mg in a sealed aluminum pan was heated from 25 °C to 190 °C at a rate of 10 °C/min and held at this temperature for 5 min. Then, the sample was cooled back to 25 °C at the rate of 10 °C/min and finally, heating of it from 25 °C to 190 °C at the same rate was performed. Before starting the tests, the heat flow and temperature of the instrument were calibrated using the standard materials, such as indium and zinc. The crystallization and melting thermograms were recorded from the cooling and second heating cycles, respectively. The melting temperature (*T<sub>m</sub>*) and crystallization temperature (*T<sub>c</sub>*) were determined from the DSC diagrams; and the percentage of crystallinity was calculated using the following equation:

$$\%X_c = \frac{\Delta H_f(\text{PE})}{\Delta H_f^\circ(\text{PE})} \times \frac{1}{w_{\text{PE}}} \times 100 \quad (1)$$

where  $\Delta H_f(\text{PE})$  is the heat of fusion for PE in the sample, and  $\Delta H_f^\circ(\text{PE})$  is the heat of fusion of 100% crystalline PE which is 287.6 J/g (Hatakeyama & Zhenhai, 1998).  $w_{\text{PE}}$  is also the weight fraction of PE.

Morphology of the typical films was studied by scanning electron microscopy (SEM, Cambridge S360), operating at an accelerating voltage of 15 kV. Before the test, the samples were cryogenically fractured in liquid nitrogen for 2 min using a glass knife and then sputter coated with a thin layer of gold to avoid electrostatic charging and poor resolution during examination. SEM micrographs were taken at a magnification of 2000×.

Typical infrared spectra of LDPE/LLDPE/TPS and PE-g-MA films were taken using a FTIR Spectrophotometer (Bruker, model Tensor27, USA). Film spectra were recorded with a resolution of 4 cm<sup>-1</sup> in the 400–4000 cm<sup>-1</sup> wave number range.

### 2.4. Property measurements

Dynamic frequency scan measurements including storage and loss moduli of the samples were conducted on a Rheometric Mechanical Spectrometer (RMS) (model Anton Paar MCR300) with geometry of the parallel plates. Complex viscosity ( $\eta^*$ ) of the molten granules of LDPE/LLDPE/TPS blends was also measured. All measurements were performed under nitrogen atmosphere in the angular frequency range of 0.1–100 (rad/s) with the strain amplitude of 1% at 190 °C.

The measurement of tensile properties, such as ultimate tensile strength (UTS) and elongation at break percentage (EB%) of the film samples was performed using a Universal Testing Machine Zwick/Roell (model Z 2.5/TH1S), according to ASTM D882. Strip form specimens were cut from the films and strained at a rate of 200 mm/min at room temperature for both machine and

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