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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.

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, Sangnitidej, & 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^3; (2) LLDPE with MFI of 0.9 g/10 min (190 °C, 2.16 kg) and a density of 0.920 g/cm^3, 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^3) 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 and the screw speed was set at 70 rpm. The blend formulations and sample codes are summarized in Table 1.

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[a]	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

[a] Reference film sample.

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_m) and crystallization temperature (T_c) were determined from the DSC diagrams; and the percentage of crystallinity was calculated using the following equation:

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

where ΔH_f(PE) is the heat of fusion for PE in the sample, and ΔH_f°(PE) is the heat of fusion of 100% crystalline PE which is 287.6 J/g (Hatakeyama & Zhenhai, 1998). w_{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 (Brucker, model Tensor27, USA). Film spectra were recorded with a resolution of 4 cm^{-1} in the 400–4000 cm^{-1} 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 (η^*) 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

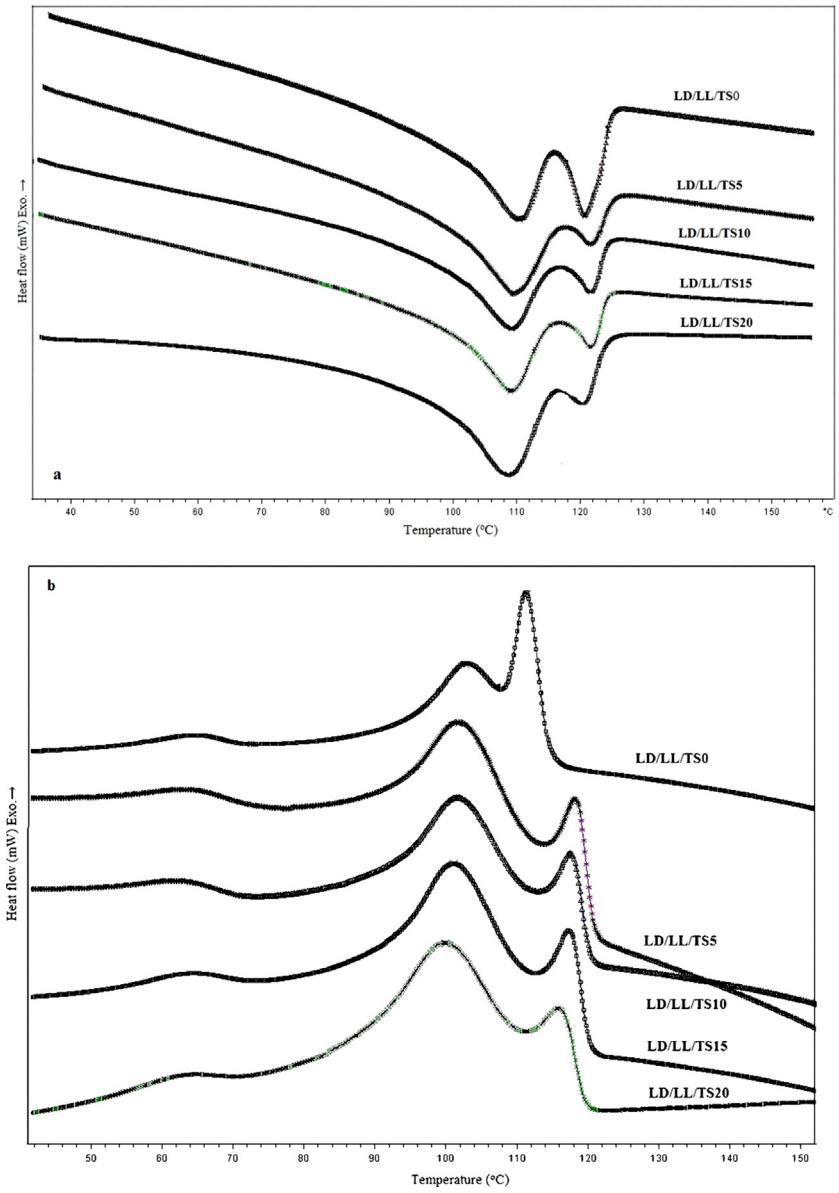

Fig. 1. DSC thermograms of LDPE/LLDPE/TPS films; (a) heating and (b) cooling cycles.

transverse directions. A Ceast free-falling dart impact tester was also used to measure the impact strength of all strip shaped film samples, according to ASTM D1709 method at room temperature. Five trials were performed for each sample and the average value was recorded.

The measurement of the haze and gloss percent of the film samples was performed on a BYK Grander GmbH apparatus in agreement with the ASTM D1003 and ASTM D2457 methods, respectively. The haze percent was evaluated by measuring the specific light transmitting of the films and was carried out on a planar section of the samples. The percentage of gloss was also conducted at angle 45° of the film surface to reflect light in a specular direction. Five readings were recorded for each sample and the average value was reported.

Water absorption of the samples was measured using 76.2 mm × 25.4 mm strips, according to the ASTM D570 method. Prior to the water absorption measurements, the samples were dried at 80 °C for 24 h in a vacuum oven. Water absorption was determined by soaking the samples in the distilled water. The oven dried weighed samples were placed inside a container filled with enough water so that the complete immersion was achieved. At regular time intervals, each sample was removed from the container, dried, and subsequently weighed to determine its water absorption. The measurements were continued until the saturation of the samples was occurred. The percentage of water absorption at any specified time (w_t, %) was calculated according to the following equation:

$$w_t\ (\%) = \left[\frac{w_2 - w_1}{w_1}\right] \times 100, \tag{2}$$

where w_1 and w_2 were the weight of dried sample and the sample after immersion at time t, respectively. The percentage of equilibrium water absorption (wt%) was calculated after water saturation in the samples.

3. Results and discussion

The heating and cooling thermograms obtained by DSC are represented in Fig. 1a and b, respectively. The degree of crystallinity (X_c), crystallization temperature (T_c) and melting temperature (T_m)

Table 2
DSC results for LDPE/LLDPE/TPS films.

Sample code	Crystallinity (%)	T_{c1}[a] (°C)	T_{c2}[b] (°C)	T_{m1}[c] (°C)	T_{m2}[d] (°C)
LD/LL/TS0	23.3 ± 4.1	101.7 ± 0.9	112.0 ± 2.1	110.9 ± 1.2	120.3 ± 1.9
LD/LL/TS5	22.5 ± 4.1	101.0 ± 1.1	117.3 ± 1.1	110.5 ± 1.2	122.0 ± 2.1
LD/LL/TS10	21.8 ± 3.6	100.5 ± 0.7	116.5 ± 1.7	110.0 ± 1.3	121.7 ± 1.7
LD/LL/TS15	20.9 ± 3.2	100.1 ± 1.0	116.2 ± 1.9	109.3 ± 1.1	121.0 ± 1.9
LD/LL/TS20	20.4 ± 4.8	99.0 ± 1.3	115.8 ± 1.2	108.2 ± 1.3	120.6 ± 1.2

[a] Crystallization temperature of LDPE.
[b] Crystallization temperature of LLDPE.
[c] Melting temperature of LDPE.
[d] Melting temperature of LLDPE.

during the second heating cycle are summarized in Table 2. Two melting peaks are observed in each sample, as it is seen in Fig. 1a. The peak appeared at 110 °C is attributed to the melting of LDPE, while another one corresponds to the melting of LLDPE which observed at 120 °C. As TPS concentration in the blends increases, no significant change in these peaks takes place. In the cooling runs there are also two indicative crystallization peaks for LDPE and LLDPE near 102 °C and 112 °C, respectively. The crystallization peak of LLDPE appears to shift toward the higher temperatures with increase in TPS content, whereas LDPE shows insignificant change (Fig. 1b). Crystallization of all the samples also shows a small peak at around 60 °C, probably associated with formation of tiny crystals in the polymers during the cooling stage (Morawiec et al., 2005). Moreover, there is a little reduction in X_c for the samples as TPS content raises (see Table 2).

On the basis of DSC thermograms, two distinct peaks indicate immiscibility and the existence of more than one type of crystal species (Kyu, Hu, & Stein, 1987; Prasad, 1998). It has been shown by X-ray and laser light scattering that in LDPE/LLDPE blends, LLDPE crystallizes first on cooling. The LDPE component then crystallizes as a secondary process; thus, each component produces separate crystals (Kyu et al., 1987; Lu & Sue, 2002; Ree, Kyu, & Stein, 1987). It is reported that the LLDPE crystals may also be more ordered in orientation than the LDPE crystals. This causes change in the properties of LDPE blending with LLDPE (Li, Li, & Qin, 2012).

In ternary LDPE/LLDPE/TPS blends prepared in this work, starch particles do not melt in the extrusion process. So, as the melt cools LLDPE would crystallize first by homogenous and heterogeneous nucleation and become a solid dispersed phase in the molten LDPE. LDPE containing starch particles would subsequently crystallize around LLDPE. It seems that incorporation of starch particles has no significant effect on the orientation order of LDPE crystals compared with LLDPE. This is associated with the long chain branching of LDPE which causes entanglements within the melt. Therefore, no significant change occurs in the crystallization peak of LDPE whereas, for LLDPE shifts to higher temperatures as TPS content increases (Fig. 1b).

It should be noted that addition of 30 wt% LLDPE to LDPE promotes the X_c of the resultant blend (i.e. LD/LL/TS0), compared with LDPE. It is supposed to be originated from the higher crystallinity of LLDPE, due to its relative linearity and short chain branches. Moreover, the lowering X_c of the samples is associated to the starch particles which hinder PE chains from close packing and forming ordered structures during the cooling process (Girija & Sailaja, 2006; Gupta, Kumar, & Sharma, 2010; Liu et al., 2003; Mir et al., 2012; Thakore, Iyer, Desai, Lele, & Devi, 1999). In the absence of starch, the material surrounding the crystalline particles is composed of amorphous phases of both polyethylenes. It is reasonable to expect the incorporation of the starch particles predominantly in the amorphous phase surrounding the crystalline particles. Starch acts as a rigid dispersed phase and reduces chain flexibility of PEs which in turn decrease the X_c values (Liu et al., 2003; Thipmanee & Sane, 2012). Therefore, as TPS content increases, the crystal capacity of PEs worsen and as a result the crystallinity of the blends decreases. The interactions between the polyethylenes and/or starch-PE in the presence of PE-g-MA as the compatibilizer would be also responsible for the obtained changes.

A typical SEM micrograph of LD/LL/TS15 sample, compared with the reference sample (i.e. LD/LL/TS0) is demonstrated in Fig. 2. It seems that there is a fairly good dispersion of starch particles in the sample (Fig. 2b). Fig. 3 shows a typical FTIR spectrum of LD/LL/TS15 sample compared to the PE-g-MA as the compatibilizer. It is seen that the characteristic peaks of the anhydride group (1716 and 1791 cm^{-1}) related to PE-g-MA is diminished in the sample and one peak observed at 1676 cm^{-1}, which is assigned to ester group (—COO) formed by the chemical reaction of anhydride group of PE-g-MA with the TPS (Oromiehie et al., 2013).

In PE/starch blends, it is necessary to reduce interfacial tension between phases by chemical modification of starch or PE. Also, use of a compatibilizer having the potential of hydrogen bonding with the hydroxyl groups of starch ensures a decrease in non-uniformity of starch particles in the blends (Gupta et al., 2010; Majid, Ismail, & Taib, 2009; Taghizadeh et al., 2013; Taguet et al., 2009; Wang et al., 2004). It has been suggested that starch plasticized by glycerol is a partially miscible mixture of glycerol-rich and starch-rich phases (Anglès & Dufresne, 2000; Taguet et al., 2009; Wilhelm, Sierakowski, Souza, & Wypych, 2003). Due to the low molecular weight of the glycerol, it migrates to the interface and forms a glycerol layer between starch and PE which in turn decreases the interfacial tension of the blend. It has been reported that PE-g-MA copolymer tends to react with the glycerol layer initially in compatibilized PE/TPS blends (Taguet et al., 2009). In the present study, 3 wt% PE-g-MA is used to enable desired compatibility in PEs/TPS blend films. It is believed that PE-g-MA has tendency to react with the TPS and is located at the interface between TPS–LDPE and/or TPS–LLDPE that improves interfacial interactions and the mechanical properties of the resultant blends.

Fig. 4a and b presents the influence of TPS loading on dynamic shear storage modulus (G') and loss modulus (G'') of the samples, respectively. In all samples, G' increases as TPS content raises. G'' increases too, but with a lower magnitude. Fig. 4c shows that as the angular frequency increases, the complex viscosity (η^*) decreases, indicating the pseudo-plastic behavior of the samples. Fig. 4c also indicates that with increasing the TPS loading, η^* of the samples increases compared to the reference (i.e. LD/LL/TS0). In polymer blends, the molecular structure of each polymer as well as the blend composition play an important role in the rheology of the blends and consequently their performance in the film blowing process (Micic & Bhattacharya, 2000). It is known that LLDPE processes more difficult than LDPE owing to high melt viscosity caused by its high short chain branches and narrow molecular weight distribution (Li et al., 2012). So, addition of LLDPE to LDPE increases the viscosity of the resulted blend. Moreover, rising trend of viscosity for the samples containing TPS could be owing to the

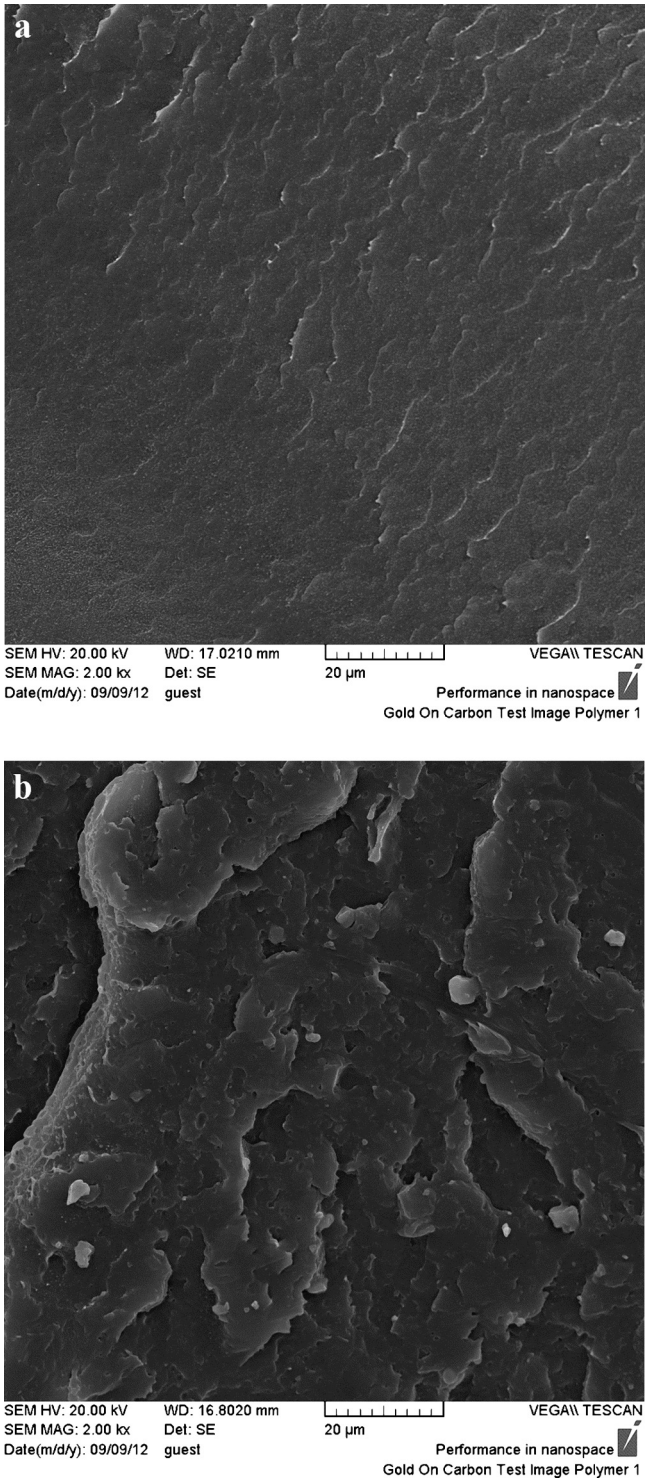

Fig. 2. Typical SEM micrographs of the films: (a) LD/LL/TS0, (b) LD/LL/TS15; magnification of 2000×.

stiffening effect of starch particles dispersed in PE matrices during the melt blending which could be intensified with higher TPS loadings (Oromiehie et al., 2013; Sabetzadeh et al., 2012). It should also be noted that probable agglomeration of starch particles in LDPE/LLDPE blend is more facilitated as TPS content increases. This causes low mobility of the polymer chains, leading to increase in η^* of the samples. Interactions between polymer components of the blends as well as starch–glycerol interactions in the boundaries could also be responsible for the changes in viscosity. The other factor affecting the viscosity of the samples would be starch stabilization effect on PE degradation (Sabetzadeh et al., 2012). LDPE forms more radicals than LLDPE during melt processing which can be attributed to a number of branching points in LDPE with loosely bound tertiary hydrogens in the polymer molecule (Andersson, Stålbom, & Wesslén, 2004). The starch melt stabilizing effect may be explained by the radical trapping action of starch particle surfaces (Bagheri, 1999; Bikiaris, Prinos, & Panayiotou, 1997). These macroradicals in the extruder cause crosslinking of the LDPE (Decker, Mayo, & Richardson, 1973) which in turn increases the viscosity (Sabetzadeh et al., 2012).

Tensile properties of the samples such as ultimate tensile strength (UTS) and elongation at break (EB%) as a function of TPS content for both machine and transverse directions are shown in Fig. 5a and b, respectively. For all samples, the tensile strength in the machine direction (MD) is higher than that in the transverse direction (TD). The elongation at break shows the opposite trend, i.e. it is lower in the machine direction than in the transverse direction. This can be attributed to the higher degree of orientation that macromolecules experience inside and outside the die in the machine direction compared to the transverse direction.

It has been found that with incorporation of LLDPE into the LDPE, the tensile properties as well as the impact strength of the resultant blend (i.e. LD/LL/TS0 as the reference) increase (Lu and Sue, 2002). It is ascribed to the higher tensile properties and impact strength of LLDPE than LDPE. Low decrease in tensile properties is observed in the LD/LL/TS5 and LD/LL/TS10 samples. Other samples show more decrease in the tensile properties. As an example, the reduction in UTS is around 42% in machine direction and that in transverse direction is more than 47% in the LD/LL/TS20 sample with respect to the reference. Moreover, decrease in the impact strength of the samples is achieved, as TPS content increases (not shown here). The obtained mechanical properties are in agreement with those reported by others (Cerclé et al., 2013; Gupta et al., 2010; Inceoglu & Menceloglu, 2013; Majid et al., 2009; Oromiehie et al., 2013; Raj, Udayasankar, & Siddaramaiah, 2004). It is indicated that the tensile properties are strongly dependent on the starch content. Indeed, TPS acts as a non-reinforcing agent and due to its poor UTS and EB% has small contribution to the tensile properties of the samples (Majid et al., 2009; Oromiehie et al., 2013; Pedroso & Rosa, 2005; Wang et al., 2004). Furthermore, it should be noted that the presence of glycerol may lead to decreasing the UTS, but it shows positive effect on stretching properties (increase in EB%) and impact strength of the samples (Inceoglu and Menceloglu, 2013; Sabetzadeh et al., 2012). It has been suggested that the probable heterogeneous dispersion of starch in the PE matrix which is intensified with higher loading of starch (i.e. larger particle size) (Pedroso and Rosa, 2005; Sabetzadeh et al., 2012) would be responsible for these changes. Because of starch particle aggregates in the interfaces of boundary layers, stress concentration occurs in the samples resulting in poor mechanical properties (Inceoglu and Menceloglu, 2013; Majid et al., 2009; Wang et al., 2004). It is believed that PE-g-MA can improve interfacial properties (lower tension) between phases and due to reducing the size of aggregates results in a fairly good dispersion of starch particles in the polymer matrices which is necessary to achieve the better mechanical properties of these blends (Cerclé et al., 2013; Majid et al., 2009; Sabetzadeh et al., 2012; Wang et al., 2004). The workers reported that insignificant reduction in tensile strength of LDPE films containing 5% TPS would be obtained when 50% LDPE-g-MA is provided to the blends (Gupta et al., 2010). The branched and crosslinked macromolecules formed by the chemical reaction between TPS and PE-g-MA probably improve interfacial adhesion and facilitate stress transfer from PE matrix to TPS as the dispersed phase (Majid et al., 2009). Other researchers have shown that a combination of interfacial modifier (PE-g-MA) and a glycerol-rich layer around the TPS particles can

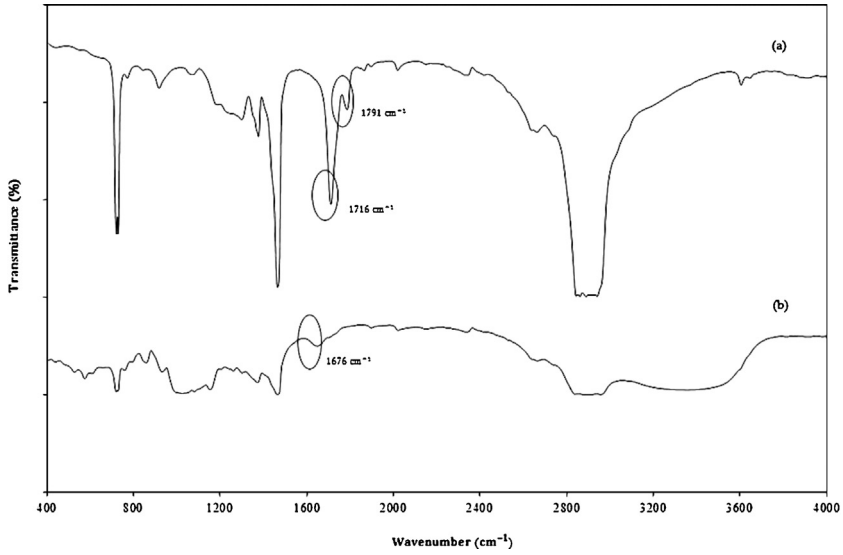

Fig. 3. FTIR spectra of (a) PE-g-MA and (b) LD/LL/TS15.

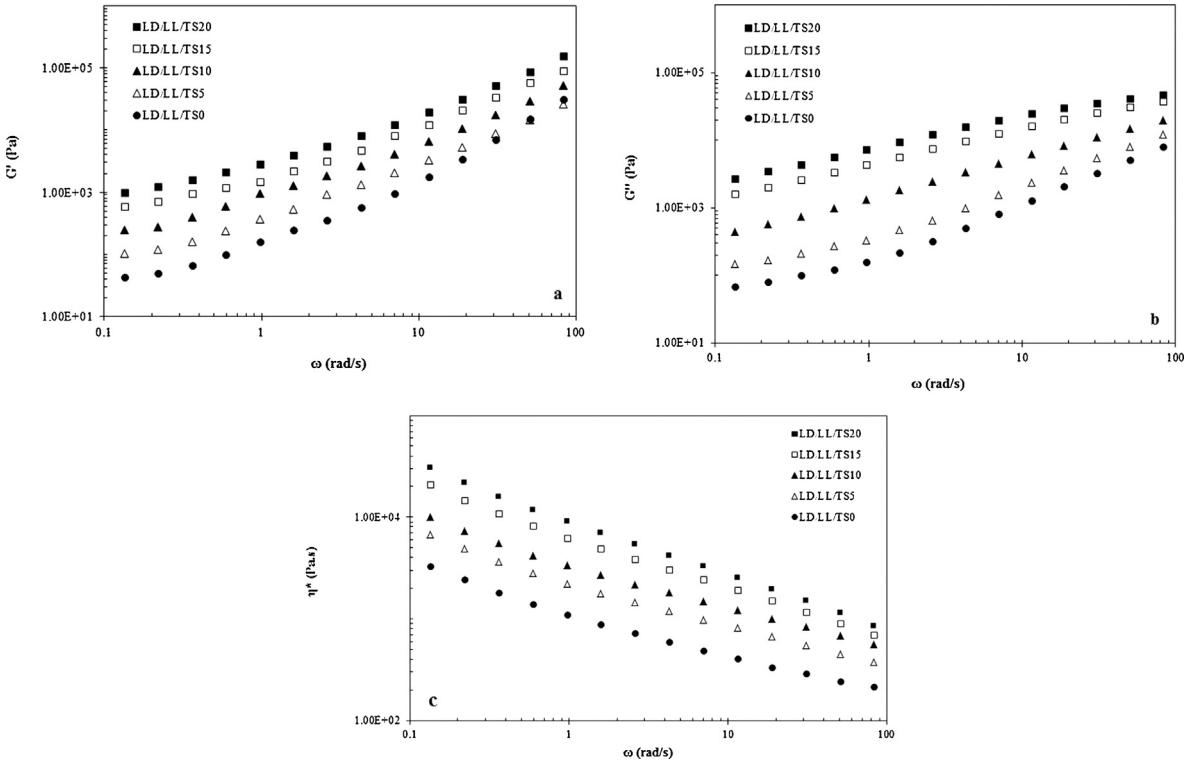

Fig. 4. (a) Storage modulus G', (b) loss modulus G'' and (c) complex viscosity η^* as a function of angular frequency (ω) for LDPE/LLDPE/TPS films, evaluated at 190 °C and 1% strain.

improve the mechanical properties of PE/TPS blends (Taguet et al., 2009). It is believed that in the present work, the highest amount of tolerated starch in the films is 15 wt% at low level of PE-g-MA. This could be noticeable compared with those reported in the literature (Gupta et al., 2010). A sample coded LD/LL/TS15 (see Table 1) fulfills the required mechanical properties for packaging applications, as evidenced by ASTM D4635 (ASTM D 4635) (UTS = 12.1 MPa, EB% = 250%).

The haze and specular gloss percent of LDPE/LLDPE films with various concentrations of TPS are summarized in Table 3. The haze property defines the specific light transmitting of the films, whereas specular gloss is a measure of the shiny appearance of them. In LD/LL/TS0 sample, incorporation of 30 wt% LLDPE leads to increase in the haze percent of the sample which is ascribed to the higher crystallinity of LLDPE. For other samples, the haze percent raises gradually after increasing the starch concentration. The results also indicate that the presence of starch is attributed to decrease in

Table 3
The haze and gloss percent of LDPE/LLDPE/TPS films.

Sample code	Haze (%)	Gloss (%)
LD/LL/TS0	18 ± 1.56	65 ± 3.6
LD/LL/TS5	21 ± 2.33	56 ± 2.9
LD/LL/TS10	26 ± 2.34	50 ± 2.7
LD/LL/TS15	31 ± 1.64	42 ± 1.1
LD/LL/TS20	38 ± 1.75	36 ± 1.3

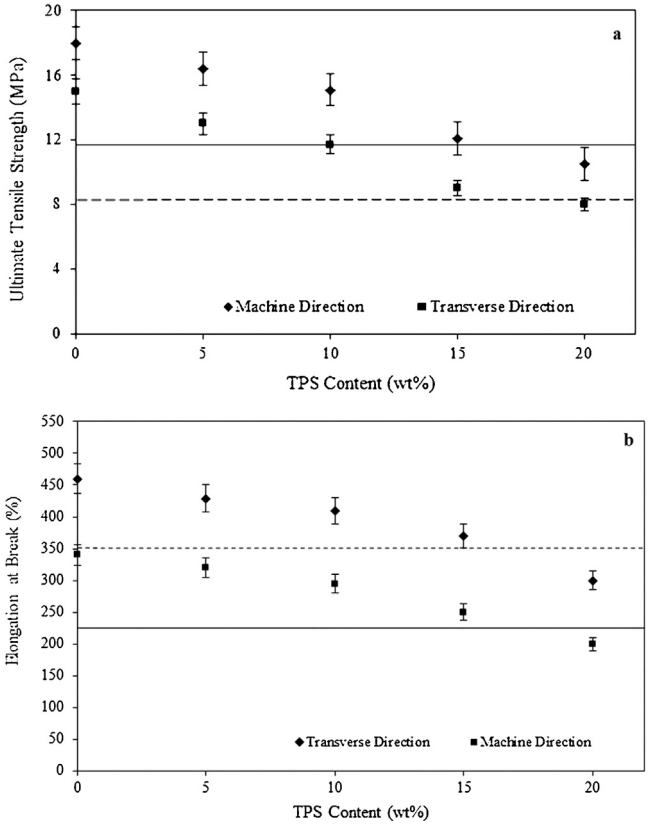

Fig. 5. Effect of TPS content on (a) ultimate tensile strength and (b) elongation at break of LDPE/LLDPE films. The threshold of the mechanical properties required for packaging applications is represented by solid line (—) for machine direction and dashed line (- -) for transverse direction.

gloss percent of the samples. Increased haze from 18% to 31% and reduction in gloss from 65% to 42% are obtained in the LD/LL/TS15 sample. The probable explanation for the observed results is the scattering/transmission of light radiation by starch, as reported for LDPE/starch films (Raj et al., 2004).

The water absorption percentage of the samples as a function of both TPS concentration and immersion time is depicted in Fig. 6. Water absorption capacity of the samples is highly dependent on the TPS content (i.e. the higher starch content, the more water absorption). Fig. 6 shows about 12% increase in the total water uptake is achieved in the case of LD/LL/TS15 sample. It can be observed that within the initial days of test, the rate of water absorption is fast, then slows down and finally reaches to the steady state value. The equilibrium content is considered as the maximum water absorption value. It is widely accepted that the existence of materials such as starch and PE-g-MA could be responsible for water absorption sensitivity of the samples. Starch as a hydrophilic polymer can facilitate water uptake of the samples by forming hydrogen bonds between water and its hydroxyl groups (Majid et al., 2009; Oromiehie et al., 2013). In addition, formation of branched or crosslinked macromolecules as a consequence of reaction between PE-g-MA and hydroxyl groups in TPS may enhance the water absorption of the samples (Majid et al., 2009; Sabetzadeh et al., 2012). It should be noted that probable microvoids between LDPE and LLDPE provide more water absorption capability, compared with PE/starch materials (Gupta et al., 2010). Increasing the water absorption due to presence of starch and/or PE-g-MA in the PE blends has also been reported by other workers (Danjaji, Nawang, Ishiaku, Ismail, & Mohd Ishak, 2002; Gupta et al., 2010; Majid et al., 2009; Oromiehie et al., 2013).

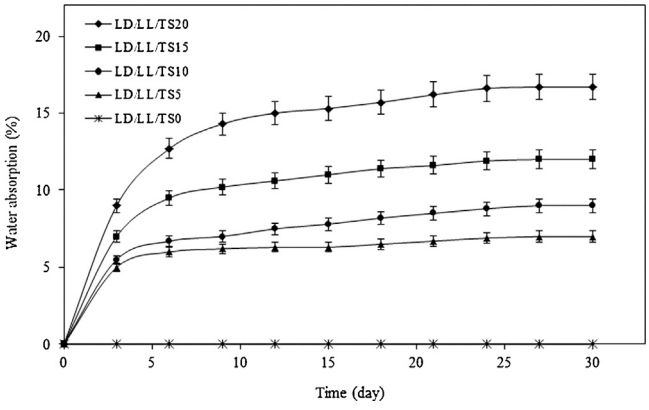

Fig. 6. Water absorption percent of LDPE/LLDPE/TPS films as a function of immersion time: effect of various composition of TPS (a day = 24 h).

4. Conclusions

Environmentally friendly materials comprising of a constant LDPE/LLDPE blend with various TPS contents using PE-g-MA as the compatibilizer are prepared in a twin screw extruder followed by a post extrusion film blowing process. Starch particles affect more prominent on crystallization of LLDPE than the LDPE, due to long chain branching of LDPE which causes entanglements within the melt. A good dispersion of starch particles in PE matrices is obtained in the presence of PE-g-MA as the compatibilizer. The characteristic FTIR peak appeared at 1676 cm^{-1} related to the ester group is due to the chemical reaction of anhydride group in PE-g-MA with the hydroxyl groups of starch which verifies compatibility between PE and TPS. The storage and loss moduli as well as the complex viscosity increase by increasing the TPS content, indicating stiffening effect of starch particles in the blends. It is claimed that the maximum content of TPS at which the required mechanical properties of PE packaging films should be maintained is 15 wt%, as specified in ASTM D4635. For this sample, increased haze from 18% to 31% and reduction in gloss from 65% to 42% are obtained, which is ascribed to the scattering/transmission of light radiation by starch. It is believed that ternary LDPE/LLDPE/TPS blend films having potential abilities in real applications will be biodegrade due to the combination effects of oxygen, bacteria, photon and humidity after usage, in favor of environment protocols.

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