Carbohydrate Polymers 82 (2010) 1082–1089

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Effects of LDPE and glycerol contents and compounding on the microstructure and properties of starch composite films☆

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ARTICLE INFO

Article history:
Received 9 February 2010
Received in revised form 16 June 2010
Accepted 18 June 2010
Available online 30 June 2010

Keywords:
Compounding
Extrusion
Films
LDPE
Properties
Starch

ABSTRACT

Corn starch–low density polyethylene (LDPE) blends, at ratios of 95:5, 90:10 and 85:15, were processed into thin films by either single-step twin-screw extrusion or by a two-step process involving compounding (pelleting) of the ingredients before film formation. The microstructure, X-ray patterns, and the tensile, thermal and water vapor permeability (WVP) properties of the films, prepared by both methods, were evaluated and compared. SEM micrographs of the single-step processed films were characterized by the presence of cracks and a discontinuous interface between starch and LDPE. Consequently, their tensile and WVP properties were impaired. Compounding, on the other hand, improved the dispersion of LDPE on to the starch matrix and the interface between the starch and LDPE phases by lowering the viscosity of the thermoplastic starch (TPS) melt. As a result, the stress transfer between the starch and LDPE phases was improved, enhancing the tensile and water vapor barrier properties of the films considerably. In general, the tensile strengths and moduli increased as the LDPE content increased from 5 to 10%, but then decreased with further increase in LDPE content to 15%. Addition of glycerol decreased the tensile strengths and moduli but did not necessarily improve the tensile strains. Differential scanning calorimetry scans and Fourier-transform infrared spectra did not indicate any significant interactions between the two immiscible polymers even after compounding. Phase separation was observed in the TPS. The water vapor barrier properties of the composites were improved by 7.3–25.4% after compounding, but were adversely affected by glycerol content.

1. Introduction

Starch is a widely used polymer in thermoplastic applications because of its biodegradability, abundant availability and low cost. Plasticized and gelatinized starch, processed at high temperatures and shear, will flow and form films like synthetic polymers. But, the hydrophilic nature of starch is a major constraint that limits the development of solely starch-containing films. To make starch-based films a greater barrier to moisture and to improve their strength and flexibility, thermoplastic starch (TPS) is blended with synthetic polymers (Swanson, Shogren, Fanta, & Imam, 1993). Starch–polyethylene, starch–poly(lactic acid), starch–poly(caprolactone), starch–polyhydroxybutyrate, starch–poly(vinyl alcohol) (PVA) and starch–poly(glycolic acid) co-polymers are commonly reported (Bastioli, Bellotti, Giudice, & Gilli, 1993). Among them, starch-filled polyethylene plastics have been widely researched (Matzions, Bikiaris, Kokkou, & Panayiotou, 2001; Otey, Westhoff, & Doane, 1980, 1987; Roper & Koch, 1990; Wang, Jiugao, & Jinglin, 2006).

Griffin (1977) first described a patented process of making starch–low density polyethylene (LDPE) blown films containing unsaturated fatty acids and their derivatives. Similarly, Otey et al. (1980) showed that starch–poly(ethylene-co-acrylic acid) mixtures containing up to 60% starch could be extrusion-blown into thin films. Later, Swanson, Westhoff, and Doane (1988) studied the effect of starch modification on starch–LDPE films containing ethylene acrylic acid (EAA), and reported that hydroxylpropylated and acetyl derivatives of starch had higher tensile strengths and elongations than those of native starch-filled films. The granular size and

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doi:10.1016/j.carbpol.2010.06.032

type of starch also influenced the physical properties of starch-filled polyethylene films (Lim, Jane, Rajagopalan, & Seib, 1992).

In composites, the starch interacts with the synthetic polymer by grafting. Chinnaswamy and Hanna (1991) prepared starch graft co-polymers by first generating free radicals on starch, and then allowing them to serve as micro-initiators for other synthetic monomers. The heat and shear in thermo-mechanical processing broke the covalent bonds in the starch to generate free radicals, which polymerized the starch with molecules containing similar synthetic polymer groups. Both C_1–C_2 and C_2–C_3 glycol groups of starch were predominant sites for initiation of graft polymerization (Doba, Rodehed, & Ranby, 1984).

When two or more polymers are present in a film, one polymer may serve as a structural component more than the other(s) depending on its structural strength, microstructural arrangement in the continuous phase and interaction with nearby polymeric domains. Starch used in composite films may either act as a filler within the network formed by the synthetic polymer (Bagley, Fanta, Burr, Doane, & Russell, 1977) or form a continuous-phase material (Otey & Westhoff, 1979).

The two major issues with composite films, and particularly those of starch–LDPE, are: (a) poor adhesion and compatibility between the hydrophilic starch and the hydrophobic synthetic polymer, which results in weak functional properties and (b) their non-biodegradability, especially at higher LDPE concentrations. In general, the degree of adhesion between the two immiscible polymers is affected by the structures of the polymers and plasticizers, compatibilizers, process temperature and applied shear.

In order to improve the compatibility of the starch–synthetic polymer blends, compatibilizers such as EAA or ethylene–maleic anhydride were added (Bikiaris, Prinos, & Panayiotou, 1997; Matzions et al., 2001). Compatibilizers reduce the interfacial energy and homogenize the polar starch with the non-polar synthetic polymer phase. Lawton and Fanta (1994) reported that addition of small amounts of EAA to cast films containing starch, PVA and glycerol improved their elongation properties. Though added in small amounts, the compatibilizers are extremely toxic. On the other hand, compounding of the starch–LDPE–plasticizer mixtures into pellets before film formation could improve the blending and dispersion of the two immiscible polymers.

Most studies cited above focused on the development and evaluation of starch–LDPE films where starch was only a minor ingredient, constituting less than 40% of the total polymers. In such films, the role of starch was mostly a filler while LDPE formed a continuous phase. However, literature on starch–LDPE films, where starch constitutes >90% and LDPE forms a minor dispersed phase, is meager. This study was unique because the starch–LDPE blends contained 85–95% starch, as compared to the level of 0–40% reported by most authors (Psomiadou, Arvanitoyannis, Biliaderis, Ogawa, & Kawasaki, 1997; Zuchowska, Steller, & Meissner, 1998). The reasoning behind this approach was that when the biodegradable component present was removed by microorganisms during waste disposal, the synthetic LDPE polymer, containing the remaining inert components, would disintegrate and disappear (Chandra & Rustgi, 1998). Hence, such composites containing high levels of starch will undoubtedly be more eco-friendly and biodegradable.

In this study, glycerol was tested as both a plasticizer and a compatibilizer to improve the interfacial adhesion between the two polymers while avoiding the common hazardous compatibilizers. The aim was to prepare a series of starch–LDPE films, varying in LDPE and glycerol concentrations, and to evaluate their microstructure, crystalline patterns and tensile, thermal and water vapor permeability (WVP) properties. In addition, the effect of compounding of the starch–LDPE–plasticizer mixtures on the film microstructure and properties was examined.

2. Experimental

2.1. Extrusion of films

Normal corn starch (Tate & Lyle Ingredients Americas Inc., Decatur, Illinois) was mixed with film-blowing grade low density polyethylene (LDPE) pellets (type 800A, Westlake Chemical Corp., Houston) at ratios of 95:5, 90:10 and 85:15, and extruded into thin films in a twin-screw extruder (model CTSE-V, C.W. Brabender Instruments Inc., New Jersey). Prior to extrusion, the moisture contents of the mixtures were adjusted to 20% (d.b.). Industrial grade glycerol (Univar USA Inc., Redmond, Washington), at 25, 30 and 35% (w/w) concentrations, was used as a plasticizer.

Before extrusion, the ingredients were mixed in a Hobart mixer (model C-100, Hobart Corp., Ohio) for 5 min and stored overnight. The feed, metering and compression sections of the extruder barrel, as well as the 100 mm wide sheeting die, were maintained at 50, 120, 120 and 115 °C temperatures, respectively. The die temperature was kept slightly below the barrel temperature to avoid boiling and bubble formation in the melt, which are detrimental to film properties. Sheeting of films was done at a screw speed of 45 rpm.

One set of samples was compounded into pellets in the same twin-screw extruder before sheeting. Compounding was done using a rod-die fitted with a circular nozzle of 3 mm diameter. The temperature profile of the extruder barrel and screw speed were maintained 40–80–80–80 °C and 50 rpm, respectively. The starch–LDPE–glycerol mixtures were fed at a rate of 40 g/min using a flex-wall volumetric feeder (PW40PLUS-0, Brabender Technologie Inc., Ontario, Canada). The extruded strands were cut into 4 mm long pellets using a rotary knife attached externally to the rod-die. The pellets were transferred to LDPE bags and sealed to avoid loss of moisture before sheeting.

In case of direct sheeting (without compounding), the granular ingredients were fed into the extruder using the flex-wall volumetric feeder. On the other hand, compounded pellets were fed through a vibratory feeder (Model DX, Eriez Manufacturing Co., Erie, Pennsylvania). The material feed rate was maintained at 50 g/min in both cases. The clearance between the two mandrels of the sheeting die was kept at 0.4 mm to obtain films of 0.4–0.5 mm thickness. The films were cut into strips of 250 mm length and dried on aluminium trays for 72 h at 20–22 °C and 50–56% RH, sealed in LDPE bags and subsequently tested.

2.2. Morphology and texture of starch–LDPE films

The microstructures of films were examined using a variable pressure SEM (model S-3000N, Hitachi High Technologies America, Inc., San Jose, California). Circular film specimens of 12 mm diameter were cut and fixed onto metal stubs with double-sided adhesive tape. The samples were sputter-coated with palladium under vacuum to render them conductive. The microscopic images were then acquired at 500× and 1000× magnifications with a resolution of 1280 × 960 pixels.

2.3. X-ray diffraction

The crystalline structures of the composite films were studied using a Bruker X-ray diffractometer (model AXS D8 Discover, Karlsruhe, Germany) as described by Pushpadass, Marx, Wehling, and Hanna (2009). The “Hi-Star” detector was mounted at a distance of 150 mm on the 2θ arm.

2.4. Tensile properties

The strain–stress characteristics of the composite films were analyzed using a universal testing machine (Model 5566, Instron

Engineering Corporation, Norwood, Massachusetts) equipped with a 2 kN load cell, at a cross-head speed of 40 mm/min. Rectangular-shaped film strips of 25 mm × 150 mm were cut with a sharp hand press, and were mounted on the jaws using filter paper grips. The tensile tests were performed according to ASTM standard D882-97, and as reported in Pushpadass et al. (2009).

2.5. Differential scanning calorimetry

The onset of glass transitions and the melting endotherms in the raw mixtures and composite films were analyzed using a differential scanning calorimeter (DSC) (model DSC822, Mettler Toledo, Columbus, Ohio). The samples were heated from −25 to 140 °C at a constant rate of 5 °C/min. The glass transition temperatures (T_g) of LDPE, in pure form and in the composites, were determined by running separate scans from −10 to −150 °C. Nitrogen gas was supplied to purge the system at a flow rate of 150 ml/min. The instrument was calibrated using indium as the standard and measurements were taken against an empty aluminium pan as the reference. Each sample was scanned at least twice and the mean values were computed. The onset of T_g and T_m of the two polymers was determined using the Star SW 8.10 software. Also, the enthalpies associated with the melting of TPS in the composites were determined.

2.6. Fourier-transform infrared spectroscopy

Fourier-transform infrared (FTIR) spectra from 4000 to 650 cm^{-1} region were obtained using an attenuated total reflectance-FTIR microscope (Smiths Detection, Danbury, Connecticut). The film samples were pressed against the objective and analyzed directly. The diffuse reflectance angle was set at 5°, and 32 scans were acquired per image at a resolution of 4 cm^{-1}. Each sample was scanned three times.

2.7. Water vapor permeability

The water vapor transmission rate and WVP were estimated gravimetrically using the modified ASTM standard E96-95 described in detail by Pushpadass et al. (2009).

2.8. Experimental design and data analyses

There were nine treatment combinations (3 levels of starch:LDPE ratios × 3 levels of glycerol) each for the direct sheeting and the two-step processing involving compounding of the ingredients prior to film formation. The extrusion experiment was laid out as a factorial design with two replications. The data on tensile and WVP properties were analyzed using the 'Proc Mixed' procedure of SAS (ver. 9.1, SAS Institute Inc., Cary, North Carolina), with the significance level of $\alpha \leq 0.05$. Duncan's multiple range test was used to compare the significant differences between the treatment means.

3. Results and discussion

3.1. Compounding and film formation

At a feed rate of 40 g/min and residence time of 4–5 min during compounding, extrusion temperatures above 80 °C melted the LDPE pellets to a large extent and produced cohesive strands. But, due to excess melting and swelling of starch, the strands obtained were expanded and sticky, which could not be cut into pellets. Conversely, extrusion temperatures below 80 °C and residence times of 4–5 min did not melt the LDPE sufficiently to produce cohesive extrudates. Therefore, compounding of the ingredients was optimized at 80 °C, which produced strands that were not sticky, and could be cut into pellets. The average moisture content of the pellets immediately after extrusion was about 10.5% (d.b.), which indicated that nearly 50% of the moisture in the original mixtures was lost during compounding.

During film formation, the thermo-mechanical forces and glycerol destroyed the structure, plasticized and homogenized the starch and provided the necessary flexibility to the films. The torque and back pressure inside the extruder while sheeting were much less for compounded samples, indicating that their viscosities were much lower than the directly sheeted mixtures. Because compounding involved greater shear, the TPS in the compounded film blends already underwent significant melting and molecular fragmentation, resulting in lower viscosities during film formation. Also, due to the plasticizing effect, the torque and back pressure during film formation decreased with increasing glycerol content in the feed mixtures.

Films extruded from the pellets were smooth, bubble-free and had a nearly transparent and sheen appearance, especially at 25 and 30% glycerol contents. On the other hand, films sheeted directly from the uncompounded mixtures of starch and glycerol were rough-textured and less flexible. The mean thicknesses of the compounded and uncompounded films were 0.47 and 0.61 mm, respectively. The directly sheeted blends were thicker because of their higher melt-viscosities inside the extruder. The moisture contents of the compounded and uncompounded films after drying were in the ranges of 3.3–4.3% and 3.5–5.1% (d.b.), respectively. Due to the vaporization of moisture while compounding, the moisture content of the films from compounded blends were at least 0.5–0.8% lower than their counterparts.

3.2. Film microstructures

The microstructures of the TPS/LDPE blends are illustrated in Figs. 1 and 2. The morphology of the composites revealed dispersion of partially melted starch granules in the film network. However, the number and distribution of native starch granules was much less in compounded film blends due to the additional thermo-mechanical processing involved. The directly sheeted films had large aggregated globules of LDPE, indicating the non-homogenous distribution of LDPE in the starch network. The distinct interface and apparent cracks between starch and LDPE in uncompounded blends were suggestive of the lack of adhesion and miscibility at the interface between the two polymers.

In contrast, the SEM micrographs of the compounded films showed an improved dispersion of LDPE in the starch phase. The LDPE globules were relatively smaller in size and uniformly distributed as a layer on the film surface, with a diffused interface with starch, and without apparent cracks (Fig. 1). This was because both polymers should have had closer viscosities so as to reduce the interfacial instabilities unlike with direct sheeting. Thus it could be stated that the compounding reduced the viscosity and increased the fluidity of the TPS inside the extruder during film formation. Rodriguez-Gonzalez, Ramsay, and Favis (2003) reported that TPS melt behaved as a typical thermoplastic material at lower viscosities and demonstrated high levels of coalescence with LDPE in such cases. In general, the thermoplastic composites were reported to have a porous texture (Griffin, 1974) because of the interfacial instability of the two polymers. However, in this study, as the pores were filled by glycerol, the film surfaces were progressively smoother with increasing glycerol content (Fig. 2a vs. Fig. 2b).

3.3. X-ray diffraction

The X-ray diffractograms summarizing the effects of compounding, as well as those of LDPE and glycerol concentrations, on the crystalline structures of the blends are presented in Fig. 3. Both

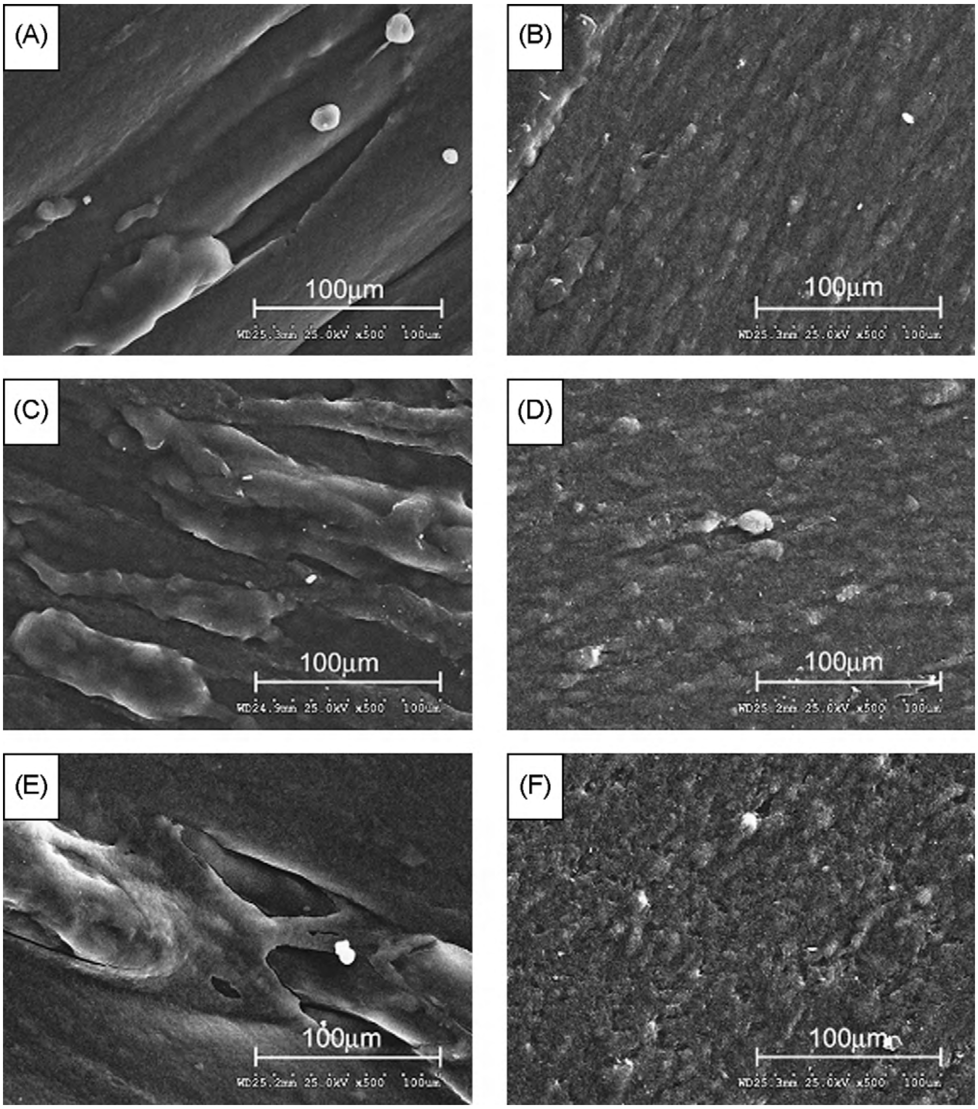

Fig. 1. Effects of compounding and LDPE content on the surface morphology of composite films plasticized with 25% glycerol and consist of (a) 95S:5PE-P, (b) 95S:5PE-NP, (c) 90S:10PE-P, (d) 90S:10PE-NP, (e) 85S:15PE-P, (f) 85S:15PE-NP (S, corn starch; PE, polyethylene; P, compounding; NP, no compounding).

types of composites manifested crystalline starch-related peaks at 2θ angles of 13.3°, 17.4°, 18.7° and 20.0°, which largely resembled a 'B'-type structure. Thus, the native 'A'-type crystalline structure of starch was lost after extrusion. The development of 'B'-type lattice structure could be attributed to the fast recrystallization of amylose or the outer chains of amylopectin, or both, in the presence of glycerol. The crystalline peak at 2θ of 20.0° was due to 'V_h' crystallinity (Hulleman, Janssen, & Feil, 1998), a single-helical inclusion complex of amylose, lipids and glycerol (van Soest & Vliegenthart, 1997) formed during extrusion.

The additional peaks at 21.6° and 23.8° were attributed to that of LDPE (Matzions et al., 2001).

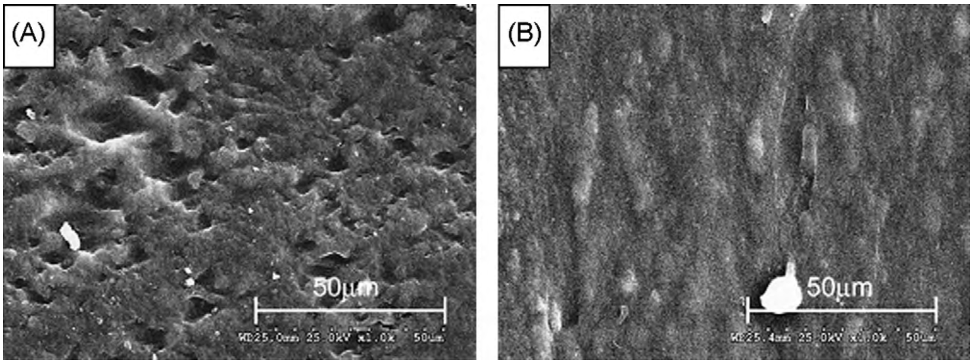

Fig. 2. Effect of glycerol content on the surface morphology of compounded films (a) 25% and (b) 35%.

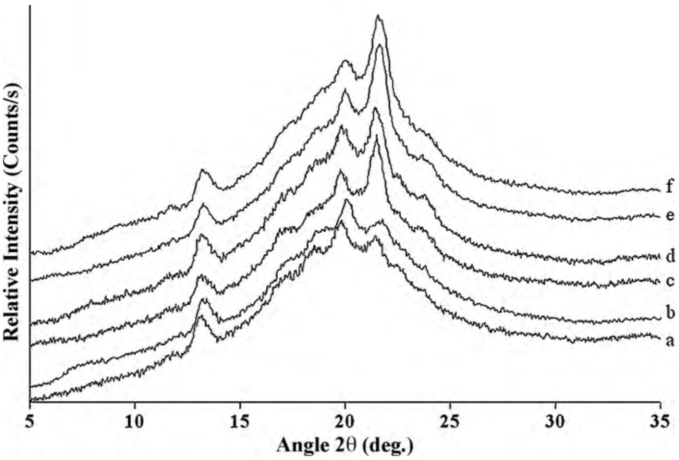

Fig. 3. X-ray patterns of (a) 95% S + 5% PE + 25% G–P, (b) 95% S + 5% PE + 35% G–P, (c) 85% S + 15% PE + 25% G–P, (d) 85% S + 15% PE + 35% G–P, (e) 85% S + 15% PE + 25% G and (f) 85% S + 15% PE + 35% G composite films (S, corn starch; PE, polyethylene; G, glycerol; P, compounding).

The intensity of the peak at 21.6° increased with increasing concentration of LDPE in the blends. This peak was absent in starch-only films containing glycerol as plasticizer (Pushpadass et al., 2009). Incidentally, the peaks related to LDPE also had relatively higher intensities in the uncompounded films (Fig. 3d and e) due to the presence of large globules of LDPE. However, no significant interactions or fusion of the starch and LDPE-related peaks were observed in the X-ray diffractograms of the films processed by both methods.

3.4. Tensile properties

The tensile strengths (max. tensile stresses), % tensile strains and moduli of composite films are summarized in Table 1. The main effects of starch, glycerol and compounding on the tensile properties were significant ($P < 0.05$). In addition, their interaction effects on the tensile properties also were significant, suggesting that the influence of one treatment (say compounding) was dependent on the levels of the other two treatments tested. The tensile strengths of both compounded and uncompounded films increased when the LDPE content increased from 5 to 10% ($P < 0.0001$), but dropped considerably with a further increase to 15%. The highest concentration of LDPE did not increase the tensile strength and moduli possibly due to more discontinuities and fissures between the starch and LDPE phases. Since the covalent linkages between starch and LDPE were not likely formed during the processing, incorporation of more LDPE produced discontinuity in the film matrix (Lim et al., 1992).

For comparison, the tensile strength and tensile strain of pure LDPE films were reported to range from 9.7 to 17.2 MPa and 500 to 725%, respectively (Shah, 1984). Such wide variations in the tensile properties of pure LDPE were attributed to their melt flow indices and actual compositions of the virgin LDPE. The manufacturer's (Westlake Chemical Corporation, Houston) specifications of tensile strength and tensile strain of the 800 A LDPE used in this study were 12 MPa and 500%, respectively. The tensile strengths and tensile strains obtained of the starch–LDPE films compared to 13.3–46.7% and 4.2–14.8% of the original values of 800 A grade LDPE. The tensile strengths and tensile strains of similarly plasticized starch-only films were 0.6–2.1 MPa and 67.3–90.8% (Pushpadass et al., 2009). It could be argued that the addition of 5–10% LDPE improved the tensile strength of the starch films considerably though the tensile strains were not improved. Psomiadou et al. (1997) reported the tensile strength and tensile strain of LDPE films as 8.34 MPa and 627%, respectively. The corresponding tensile strength and tensile strain decreased to 4.7 MPa and 73% when starch was blended with LDPE at 40:60 ratio. Similarly, Zuchowska et al. (1998) obtained tensile strengths and tensile strains of 3.8 MPa and 16.3% and 7.5 MPa and 49.3%, respectively for 40:60 and 70:30 LDPE-starch blends plasticized with 30% glycerol. The moduli of the starch–LDPE film were quite high because of the stiffening effect caused by intermolecular cohesive forces and direct interactions of the starch granules after extrusion (Zhang & Han, 2006).

The tensile properties of the films were enhanced greatly by compounding ($P < 0.0001$). The differences in the tensile properties between the compounded and uncompounded blends were attributed to the degree of dispersion and blending of LDPE within the starch network. When there was no proper interface between the matrix and LDPE, as in uncompounded films, the tensile properties suffered due to the lack of transfer of the applied load across the starch–LDPE interface (Evangelista, Nikolov, Sung, Jane, & Gelina, 1991). It would be easy for large chunks of LDPE to initialize craze in uncompounded films, which would have cracked and resulted in fracture at significantly lower tensile loads. On the other hand, compounding increased the interfacial area between starch and LDPE considerably, which helped to transfer the applied load and achieve higher tensile strengths, strains and moduli.

Table 1
Tensile and water vapor permeability properties of starch–LDPE composites.

Starch:LDPE ratio	Glycerol (%)	Compounding	Tensile strength (MPa)	Tensile strain (%)	Modulus (MPa)	WVP (g mm/h m^2 kPa)
95:5	25	–	4.8c	30.0e	247.6b	9.7abc
95:5	30	–	2.8ef	54.7bcd	97.6ef	10.1ab
95:5	35	–	2.2g	51.0cd	46.8hg	10.4a
90:10	25	–	4.9c	22.1e	272.3ab	9.0abcd
90:10	30	–	2.7f	48.5cd	97.6ef	9.3abcd
90:10	35	–	1.8ij	51.7cd	32.1h	8.6bcde
85:15	25	–	4.1d	21.0e	156.4cd	9.0abcd
85:15	30	–	2.0ghi	56.0bc	34.2h	8.4cd
85:15	35	–	1.6j	43.0d	24.2h	9.2abcd
95:5	25	P	5.6ab	49.2cd	300.1a	8.3defg
95:5	30	P	3.2e	64.5ba	117.2de	9.1abcd
95:5	35	P	2.8ef	74.0a	67.5fgh	9.5abc
90:10	25	P	5.8a	44.1d	312.1a	6.8g
90:10	30	P	4.0d	63.7ab	155.4cd	7.0fg
90:10	35	P	2.9ef	54.0bcd	87.3efg	7.3efg
85:15	25	P	5.2c	51.2cd	183.6c	6.8g
85:15	30	P	2.2g	72.0a	51.8fgh	7.8defg
85:15	35	P	1.9hij	54.6bcd	25.2h	8.0defg

Means with the same letter within a column are not significantly different ($P > 0.05$) by Duncan's multiple range test; *P*, compounding.

Table 2
Thermal properties of starch–LDPE composites.

Starch:LDPE ratio	Glycerol (%)	Compounding	Moisture content (%)	Starch				T_m of LDPE (°C)
				T_{g1} (°C)	T_{g2} (°C)	T_m (°C)	Enthalpy (J/g)	
95:5	25	–	5.1	0.9	11.8	31.9	0.8	106.8
95:5	30	–	4.2	0.6	10.6	29.5	0.9	106.3
95:5	35	–	3.8	0.3	10.7	33.1	0.3	105.0
90:10	25	–	4.2	0.9	10.7	29.5	0.7	107.2
90:10	30	–	3.7	0.8	11.5	29.6	0.9	107.3
90:10	35	–	4.0	0.3	10.7	36.7	0.2	105.0
85:15	25	–	5.0	1.0	11.9	29.1	1.4	106.5
85:15	30	–	3.5	0.8	11.4	32.6	0.6	107.7
85:15	35	–	4.0	0.4	10.6	35.7	0.3	106.4
95:5	25	P	4.3	0.7	12.5	28.8	0.4	106.5
95:5	30	P	3.4	0.5	11.3	29.5	0.2	105.4
95:5	35	P	3.3	0.9	12.2	31.0	0.3	107.3
90:10	25	P	3.5	0.9	11.8	28.1	0.3	106.4
90:10	30	P	3.0	0.9	11.8	31.5	0.2	106.2
90:10	35	P	3.4	0.5	11.6	31.4	0.2	105.9
85:15	25	P	4.3	0.8	12.5	26.7	0.7	107.3
85:15	30	P	3.0	0.8	12.0	31.1	0.3	107.3
85:15	35	P	3.4	0.6	11.3	31.2	0.2	107.4

P, compounding.

In general, the tensile strength and modulus of the films decreased significantly with increasing concentrations of glycerol ($P < 0.0001$) while the % tensile strain increased. The highest values of tensile strengths and moduli were obtained at lowest (25%) glycerol contents. Dole, Avérous, Joly, Della Valle, and Bliard (2005) reported that increasing concentrations of glycerol up to 18% improved the adhesion between starch and LDPE in multilayered films. The decreasing values of tensile strengths and moduli with increasing concentrations of glycerol were attributed to the increased free volume in the film network resulting in weakened interactions between the starch chains (Lourdin, Bizot, & Colonna, 1997; Myllärinen, Partanen, Seppala, & Forssell, 2002). In addition, the higher concentrations of glycerol might have led to phase separation of starch, which created a weak boundary layer between starch and LDPE.

3.5. Glass transition and melting characteristics of composites

DSC was used to discern the glass transitions, as well as, to gain some insight into the compatibility between starch and LDPE. The DSC scans of the composites, in the temperature range tested, showed two glass transitions and two melting endotherms. The first transition in the temperature range of 0.3–1.1 °C was assigned to that of glycerol-rich regions while the second transition at 10.6–12.2 °C was related to the starch-rich domains of the TPS (Table 2). The occurrence of more than one glass transition indicated phase separation in the TPS.

The two T_g's of native corn starch plasticized with 5% moisture and 25–35% glycerol (resembling the final composition of the films) were recorded at −1 to 0 °C and 10–12 °C, respectively. The T_g's of starch-rich regions in the compounded blends were significantly higher than those observed for uncompounded blends due to the relatively lower moisture contents of the compounded blends, and possibly due to loss of some glycerol during the compounding step. The T_g of pure LDPE, run through the separate scan, was observed as −148 °C, which did not change significantly in the composites.

The presence of melting endotherms in all blends also confirmed the SEM results that the native starch granules were not completely melted and gelatinized during film formation. The native starch granules present in the TPS melted at much lower temperatures (28.1–36.7 °C) than that expected of normal corn starch. The below-normal melting temperatures (T_m) of the TPS suggested that the starch granules, as seen in SEM micrographs, were probably melted and gelatinized partially. The melting enthalpies of the TPS in the directly sheeted samples were considerably higher those of the compounded blends.

Pure LDPE melted at 111.4 °C, while in the composites LDPE melted at 105–107.3 °C. The reduction in the T_m of LDPE in the composites was suggestive of a possible weaker binding of LDPE with starch. Else, the lowering of melting point of LDPE in the composites could be due to the processing effect in the extruder. However, the melting points of LDPE had no significant differences among the blends. It could be argued the two polymers could not have compatibilized at the molecular scale. Even with EVA as compatibilizer, Prinos, Bikiaris, Theologidis, and Panayiotou (1998) did not observe any significant miscibility of starch and LDPE in their blends.

3.6. Fourier-transform infrared spectroscopy

The FTIR spectra of LDPE, native starch, starch–glycerol film and composite films in the wave numbers of 4000–650 cm^{-1} are summarized in Fig. 4. Pure LDPE showed accentuated peaks at 2914–2847 (CH stretching), 1751 (carbonyl group possibly due to oxidation), 1464 (CH_3 bending), 1377 and 719 cm^{-1} (skeletal vibration of CH_2). The spectral bands and wave numbers of LDPE were in

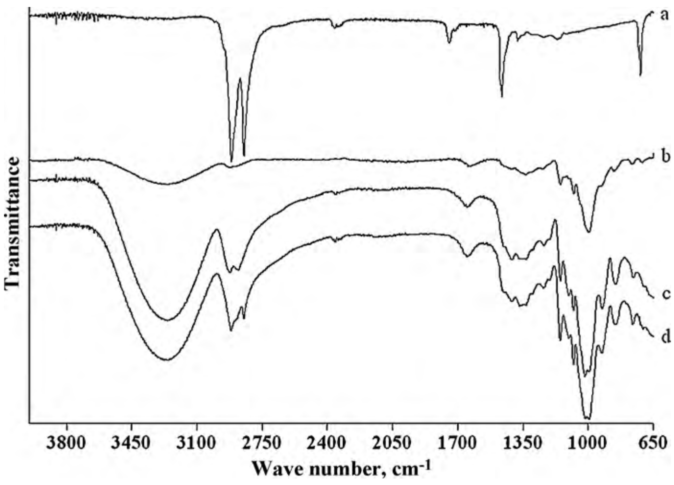

Fig. 4. FTIR spectra of (a) LDPE, (b) native corn starch, (c) starch–glycerol film and (d) starch–LDPE composite film.

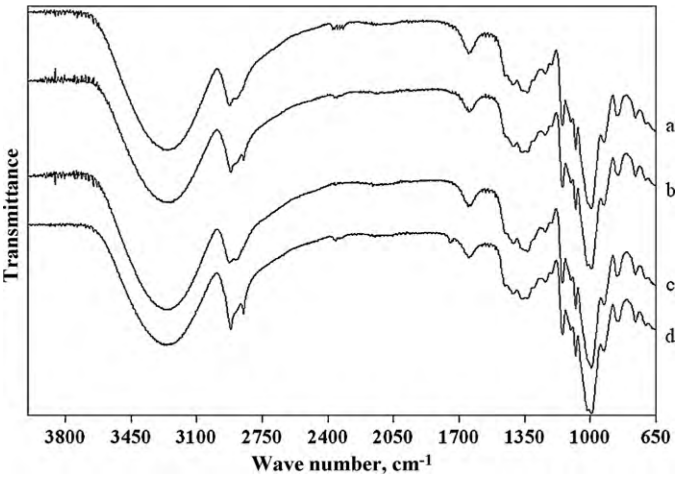

Fig. 5. FTIR spectra showing the effect of compounding on composite films containing (a) 95% S + 5% PE + 25% G, (b) 95% S + 5% PE + 25% G–P, (c) 85% S + 15% PE + 25% G and (d) 85% S + 15% PE + 25% G–P (S, corn starch; PE, polyethylene; G, glycerol; P, compounding).

general agreement with the results of Chandra and Rustgi (1997) and Raj, Sankar, and Siddaramaiah (2004).

The LDPE-related appeared in the composite films at the same wave numbers (2916, 2847 and 721 cm^{-1}), clearly indicating the absence of any significant interaction with starch (Fig. 4c vs. Fig. 4d). Also, no merging of LDPE-related peaks with those of starch was observed in the spectra. The intensities of the 2914–2847 cm^{-1} band increased with increasing concentration of LDPE in the compounded films and not in the directly sheeted samples (Fig. 5a and c vs. Fig. 5b and d). It could be inferred that the LDPE was dispersed uniformly on to the starch matrix due to compounding.

Native starch and TPS, on the other hand, had distinctive bands at 3296–3282, 2951–2895, 1666, 1420, 1373–1340, 1151, 1079, 1053 and 1022–1002 cm^{-1}, and at similar frequencies (Fig. 4b–d). The significant transformation in the spectra of TPS in two-step processed films was observed in the 1022–1002 cm^{-1} region. The peak intensity at 1022 cm^{-1}, relative to 1002 cm^{-1}, was much higher in the compounded samples as compared with those of the directly sheeted films. Since the intensity at 1022 cm^{-1} was characteristic of amorphous content in starch, it could be stated that the shear experienced during compounding may have caused fragmentation of starch and destroyed its crystalline structure.

3.7. Water vapor permeability of composite blends

The WVP of composite films were influenced markedly by compounding and LDPE contents ($P < 0.0001$). On the other hand, the effect of glycerol on water permeability was close to significance ($P = 0.041$). The interactive effects involving LDPE, glycerol and compounding were not significant, indicating that the effects of these variables on WVP were essentially linear. The WVP of the composite blends ranged from 6.8 to 10.4 g mm/(h m^2 kPa) (Table 1) as compared to the values of 12.0–19.0 g mm/(h m^2 kPa) for similarly plasticized starch–glycerol films (Pushpadass et al., 2009). The water barrier property increased when the LDPE content increased from 5 to 10%, but it did not improve with further increase in LDPE content to 15%. The WVP of two-step processed films, when compared to those of directly sheeted ones, were lower by 7.3–25.4%. Though not to expected levels, compounding decreased the WVP due to the uniform dispersion of LDPE in the starch phase.

It is well-known that glycerol adversely affects the water vapor barrier of starch films. However, glycerol was needed at 25–35% to avoid cracking of the starch (Gontard, Guilbert, & Cuq, 1993) and starch–LDPE composite films (Zuchowska et al., 1998) during handling and storage. The effect of glycerol on the hydrophobic property of starch–LDPE blends is shown in Table 1. In most cases, as the glycerol content increased from 25 to 35%, the water vapor barrier property decreased significantly. Such decreases in the water vapor barrier properties with the increasing glycerol content were reported previously (Gontard et al., 1993). However, the effect of glycerol as a plasticizer at concentrations below 25% could not be studied as the films would be brittle. The minimum level of plasticizer required for starch films was about 20% (Pushpadass et al., 2009).

4. Conclusions

Compounding and glycerol content were the main factors that influenced the film properties. SEM micrographs of the films showed that there was no miscibility between the two polymers. The X-ray patterns and FTIR spectra of the composite films were not conclusive of any strong interaction between starch and LDPE. Compounding significantly improved the film properties due to better dispersion of LDPE on the starch phase, as well as, due to the diffused interface between the two immiscible polymers. The continuity between the starch and LDPE phases and the stress transfer at their interfaces were improved after compounding. The highest tensile strengths and moduli were obtained in composite films containing starch and LDPE at 90:10. Increase in LDPE content beyond 10% did not improve the tensile properties further even after compounding. Blends with 25% glycerol content retained good functional properties. Increasing concentrations of glycerol decreased the tensile strength and moduli but did not necessarily increase the tensile strains of the films.

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