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

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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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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