



Effect of nanoclay on the properties of low density polyethylene/linear low density polyethylene/thermoplastic starch blend films



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ABSTRACT

The aim of this work is to study effect of nanoclay (Cloisite®15A) on morphology and properties of low-density polyethylene/linear low-density polyethylene/thermoplastic starch (LDPE/LLDPE/TPS) blend films. LDPE/LLDPE blend (70/30 wt/wt) containing 15 wt.% TPS in the presence of PE-grafted maleic anhydride (PE-g-MA, 3 wt.%) with 1, 3 and 5 phr of nanoclay are compounded in a twin-screw extruder and then film blown using a blowing machine. Nanocomposites with intercalated structures are obtained, based on the X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies. However, some exfoliated single platelets in the samples are also observable. Scanning electron microscopic (SEM) images confirm the ability of both exfoliated nanoclay and PE-g-MA to reduce the size of TPS domains and deform their particles within the PE matrices. As the nanoclay content increases from 1 to 5 phr, the tensile strength, tear resistance and impact strength of the films increase, whereas a slight decrease in the elongation at break is observed. The film samples with 5 phr nanoclay possess the required packaging properties, as specified by ASTM D4635. These films provide desired optical transparency and surface roughness which are more attractive for packaging applications.

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1. Introduction

Low density polyethylene/linear low density polyethylene (LDPE/LLDPE) blend films with a combination of good processability and superior mechanical properties have attracted much attention in packaging applications (Hemati & Garmabi, 2011). However, raising the problem of environmental pollution related to the accumulation of plastic packaging wastes has caused increasing interest in the use of polymers from renewable resources (Liu et al., 2014; Mortazavi, Ghasemi, & Oromiehie, 2014). Among them, starch is a natural, renewable and inexpensive polymer which can be added to polyethylene (PE) to produce environmentally friendly materials (Kahar, Ismail, & Othman, 2012; Sabetzadeh, Bagheri, & Masoomi, 2012). It is known that native starch-PE materials without a plasticizer and a modifying agent show poor processability and inferior mechanical performance, leading to limit their applications (Sharif, Aalaie, Shariatpanahi, Hosseinkhanli, & Khoshniyat, 2013; Thipmanee & Sane, 2012). Starch can be modified in the presence of a plasticizer (such as glycerol) at high temperatures (i.e. TPS) to be processed by conventional plastic-forming equipments and

also disperse fairly uniform in the polymer matrix, which is critical for mechanical properties. Several studies have been conducted on PE blends obtained with addition of TPS (Guzmán & Murillo, 2015; Mortazavi, Ghasemi, & Oromiehie, 2013; Taghizadeh, Sarazin, & Favis, 2013). Even so, these materials have a relatively high interfacial tension arises from the incompatibility between the non-polar PE and the high polar TPS, resulting in poor mechanical properties (Alidadi-Shamsabadi, Behzad, Bagheri, & Nari-Nasrabadi, 2015; Cerclé, Sarazin, & Favis, 2013). In order to overcome the incompatibility issue and as a consequence improvement in mechanical properties, addition of a suitable interfacial modifier containing reactive groups [e.g. polyethylene-grafted maleic anhydride (PE-g-MA)] has been suggested (Prachayawarakorn, Sangnitdej, & Boonpasith, 2010; Taguet, Bureau, Huneault, & Favis, 2014). Anyway, the problem of poor mechanical properties in the blends could not be properly overcome (Inceoglu & Menciloglu, 2013).

It should be underlined that inclusion of a small amount of nanofiller in a polymer blend provides a composite material with improved mechanical properties (Kim & Cha, 2014). Among inorganic compounds, more attention has recently been paid to clay minerals, especially montmorillonite (MMT) in the research area of nanocomposites, attributed to their environmentally friendly nature, small particle size, high surface area and intercalation properties. The surface of the MMT is modified with certain organic modifiers (e.g. alkylammonium cation) to provide it more

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compatible with the non-polar polymers. It is well established that surface treatment and the blending process can significantly facilitate dispersion of clay nanoparticles (Kampeerappun, Aht-ong, Pentrakoon, & Srikulkit, 2007; Ludueña, Vázquez, & Alvarez, 2013; Schlemmer, Angélica, & Sales, 2010).

In the last few years, increased interest has appeared in PE/starch blends containing clay nanoparticles. Metallocene-catalyzed polyethylene (m-PE)/TPS nanocomposites has been prepared with incorporation of clay reinforced nanocompatibilizer (Chiu, Lai, & Ti, 2009). Moreover, nanocomposites based on high-density polyethylene (HDPE)/TPS blends have been studied. It has been demonstrated that addition of nanoclay is in favor of developing nanocomposites with better performance than the native blends (Sharif, Aalaie, Shariatpanahi, Hosseinkhanli, & Khoshniyat, 2011). Besides above, low-density polyethylene (LDPE)/starch nanocomposites have been investigated. The most considerable improvement in all properties is achieved in the presence of both clay and compatibilizer (Inceoglu & Menciloglu, 2013; Manjunath & Sailaja, 2014). Our studies also suggest that LDPE/TPS blends containing nanoclay have desired mechanical properties that would be appropriate for packaging applications (Sabetzadeh, Bagheri, & Masoomi, 2014). Recently, HDPE/TPS nanocomposite films have been developed using new compatibilizer systems based on the other clay minerals such as sepiolite (Mir et al., 2013; Samper-Madrigal, Fenollar, Dominici, Balart, & Kenny, 2015; Yasin, Nisar, Shafiq, Nho, & Ahmad, 2013).

To date, ternary LDPE/LLDPE/starch blends filled with nanoparticles have rarely been reported in the literature. The present work centers around the use of a nanoclay in a compatibilized LDPE/LLDPE blend film containing 15 wt.% TPS which has been demonstrated to be suitable for packaging applications (Sabetzadeh, Bagheri, & Masoomi, 2015). The detailed effect of nanoclay addition on the morphology, mechanical properties, film characteristics such as optical transparency and surface roughness as well as water absorption capacity is investigated.

2. Experimental

2.1. Materials

Low density polyethylene (LDPE) with a density of 0.921 g/cm³, melt flow index (MFI) of 0.75 g/10 min and linear low density polyethylene (LLDPE) with a density of 0.920 g/cm³, MFI of 0.9 g/10 min (at 190 °C, 2.16 kg load) were both film grades and purchased from Petrochemical Commercial Company, Iran. The unmodified corn starch (30 wt.% amylose and 70 wt.% amylopectin) was supplied by Glucosan Company, Iran. Glycerol (99.5% purity) was reagent grade from Hansa Group AG, Germany. Polyethylene grafted-maleic anhydride (PE-g-MA, 1% grafted) was obtained from Pluss Polymers Co, Ltd (India) and used as a compatibilizer. The modified montmorillonite (Cloisite® 15A) was obtained from Southern Clay Products, Inc. (USA).

2.2. Sample preparation

All components were dried in a vacuum oven at 80 °C for 24 h prior to further treatments. 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 cm³) at 140 °C with rotor speed of 60 rpm for 8 min.

LDPE/LLDPE (70/30 w/w) blend with 15 wt.% prepared TPS in the presence of 3 wt.% PE-g-MA (Sabetzadeh et al., 2015) were melt-mixed with various contents of nanoclay (1, 3 and 5 phr) using 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 145–180 °C (from feed zone to die) and the screw speed was set at 150 rpm. The prepared compounds 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 nine zones. The barrel temperature range was 155–170 °C and the screw speed was set at 70 rpm. The prepared films designated as nbf0, nbf1, nbf3 and nbf5; containing 0, 1, 3 and 5 phr nanoclay, respectively.

2.3. Characterization and measurements

X-ray diffraction of the film samples was conducted using a Bruker D8 Advance X-ray diffractometer (Bruker, Germany) with Cu *K*α radiation ($\lambda = 0.154$ nm) at a voltage of 40 kV and 30 mA. Scattered radiations were detected in the range of diffraction angle $2\theta = 2\text{--}10^\circ$ with the scan rate of 1°/min at room temperature. The basal spacing of the nanoclay, *d*, was calculated using the Bragg equation, $d = \lambda / 2 \sin(\pi\theta / 180)$, where θ is the diffraction angle and λ is the wavelength.

A typical transmission electron microscopy (TEM) image was captured using a Phillips CM200 transmission electron microscope operating at an acceleration voltage of 200 kV. Ultrathin cut (80 nm) from the film sample, using a diamond knife under cryogenic conditions at –100 °C was performed.

Scanning electron microscope (SEM, TESCAN model Vegall), operating at an accelerating voltage of 15 kV was used to study phase morphology of the film samples. Before the test, the film samples were cryogenically fractured in the liquid nitrogen and then sputter coated with a thin layer of gold to avoid electrostatic charging and poor resolution during examination. SEM micrographs of the fracture surfaces were taken at the magnification of 10,000×.

Tensile properties, such as ultimate tensile strength and elongation at break percentage of the film samples were measured 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 cross-head speed of 200 mm/min at room temperature for both machine and transverse directions. The grip separation was set at 50 mm. Tear resistance of the films was also measured in both machine and transverse directions according to ASTM D 1922 standard test method, using a Ceast ED 300 tear tester (Elmendorf type). The average force required to propagate a tear through a specified length of the film with respect to the thickness determines the tear resistance. In addition, a Ceast falling dart impact test equipment (model 9340) was used to measure the impact strength of the strip shaped film samples, according to ASTM D1709 method at room temperature. The energy that causes films to fail under the specified conditions of impact of a free-falling dart determines the impact strength. For all mechanical tests, at least five replicates were examined for each sample and the average values were determined.

To evaluate some film characteristics, the optical transparency was determined by the light transmission rate through the films at wavelengths from 400 to 800 nm, using a UV-vis spectrophotometer (Jasco, V550 Series, Japan). Moreover, the surface roughness of the films was examined by atomic force microscopy (AFM, Bruker, Germany) at room temperature. Contact mode was used and the scanning range was 42 μm × 42 μm in at least five areas for each film sample to calculate the average (R_a) and root mean square roughness values (R_q). These are the useful tools to get information about the particle size and distribution of the clay within the blend matrix.

In order to study water absorption behavior of the film samples, they were immersed in the distilled water, according to the ASTM

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