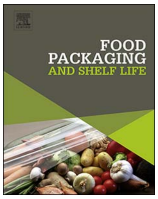
Food Packaging and Shelf Life 13 (2017) 20–26

Contents lists available at ScienceDirect

Food Packaging and Shelf Life

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



Rheological, structural, ultraviolet protection and oxygen barrier properties of linear low- density polyethylene films reinforced with zinc oxide (ZnO) nanoparticles

Jasim Ahmed[a,*], Yasir Ali Arfat[a], Hassan Al-Attar[a], Rafael Auras[b], Mohammad Ejaz[a]

[a] Food and Nutrition Program Environment & Life Sciences Research Center, Kuwait Institute for Scientific Research, P.O. Box 24885, Safat 13109, Kuwait
[b] The School of Packaging, Michigan State University East Lansing, MI, USA

ARTICLE INFO

Keywords:
Nanocomposite
Time-temperature superposition principle
Elongation at break
X-ray diffraction

ABSTRACT

Linear low-density polyethylene (LLDPE) and zinc oxide (0–10%, w/w) nanocomposite (NC) films were produced through melt-mixing extrusion process. Both LLDPE and LLDPE/ZnO NC exhibited predominating liquid-like property in the lower frequency range, however, a distinct gel point was detected at higher frequency. At 10% loading of ZnO to LLDPE followed the time-temperature-superposition (TTS) principle adequately in the selected temperature range (140–170 °C). Tensile strength (TS) of the NC increased whereas the elongation at break (EAB) decreased with increasing loading concentration of ZnO. NC films showed lower transparency, b*-values (yellowness), and ΔE*-values (total color difference) than the control LLDPE film. Incorporation of ZnO improved the ultraviolet (UV) barrier properties whereas the oxygen transmission rate decreased significantly from about 11,000 to 8000 $cm^3/(m^2\ 24\ h)$. X-ray diffraction (XRD) analysis confirmed the crystalline structure of the NC films, and an improvement in thermal stability was detected through thermogravimetric analysis. Scanning electron microscopy (SEM) exhibited well dispersion of nanoparticles in the NC matrix with a coarse film surface. Thus, LLDPE/ZnO nanocomposite films could be used as a food packaging material to prevent oxygen and UV induced lipid oxidation in food materials.

1. Introduction

Polyethylene is one of the most widely used polyolefins in the packaging industry for food packaging, agricultural film, and garbage bags due to its attractive combination of a low production cost, low-density, acceptable heat distortion temperature, chemical inertness, and easy processability (Niknezhad & Isayev, 2013). High-density polyethylene (HDPE), low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) are typically used in film manufacturing. However, advantages during manufacturing process and film properties of LLDPE make it a polymer of choice. Although the LLDPE have revolutionized the food industry and possess numerous advantages, their major limitation is high oxygen permeability and poor UV absorption properties (Duncan, 2011; Mulla et al., 2017). Development of polymeric materials with good thermal, optical, UV and oxygen barrier with improved mechanical properties has attracted much attention during the last few years. Therefore, improvements in properties of polyethylene will be beneficial for the many applications, in particular packaging of food products which are very sensitive to oxygen and UV light.

The incorporation of nanoparticles as fillers in polymers has attracted considerable interest due to the ability to achieve exceptional property enhancements at low loading levels, in particular enhancements in thermal, mechanical and barrier properties. Furthermore, these nanocomposites can act as an antimicrobial packaging system by inhibiting the growth of spoilage and pathogenic microorganisms, generally by direct contact with microorganisms or by releasing of nanoparticles with antimicrobial properties (Emamifar, Kadivar, Shahedi, & Soleimanian-Zad, 2011; Espitia et al., 2013). Nanocomposite materials are two phase systems that comprise of a polymeric matrix and organic/inorganic filler with at least one dimension on the nanometre scale (Alebooyeh, Nafchi, & Jokar, 2012; Arfat, Benjakul, Prodpran, Sumpavapol,- & Songtipya, 2016). Recently, the incorporation of ZnO nanoparticles as functional filler into the polymer matrix such as protein based films have been reported to improve mechanical and barrier properties (Arfat, Benjakul, Prodpran, Sumpavapol, & Songtipya, 2014). ZnO is currently listed as a generally recognised as safe (GRAS) material by the Food and Drug Administration (21CFR182.8991), and has previously shown strong

---

* Corresponding author.
E-mail addresses: jaahmed@kisr.edu, jahmed2k@yahoo.com (J. Ahmed).
URL: http://mailto:jaahmed@kisr.edu.kw (J. Ahmed).

http://dx.doi.org/10.1016/j.fpsl.2017.04.005
Received 10 September 2016; Received in revised form 27 March 2017; Accepted 4 April 2017

antimicrobial activity against food borne pathogens and spoilage bacteria (Espitia et al., 2013). However, limited information is available on rheological, oxygen barrier and UV-protecting properties of LLDPE/ZnO based nanocomposite films. The primary objective of this work was to elucidate the influence of ZnO nanoparticles on the mechanical, thermal, rheological, structural and barrier (UV and oxygen) properties of LLDPE films prepared by melt extrusion.

2. Materials and methods

2.1. Chemicals

A commercial grade linear low-density polyethylene (LLDPE) (EFDC-7087; Melt Index 1; density 0.92; Melting Point 124 °C) was procured from Equate Petrochemical Co. (Kuwait). ZnO nanoparticles (particle size: < 100 nm) was purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Extrusion of LLDPE films

Before actual nanocomposite film preparation, masterbatches were made by well-mixing ZnO NPs into LLDPE polymer to produce compounded pellets. To obtain a masterbatch, ZnO NPs and LLDPE granule were mixed in the weight ratio of 1:9 through a mixer, and then the blend was extruded using a twin-screw extruder (Century ZSK-30; Coperion GmbH, Germany) with a screw length/diameter (L/D) ratio of 42, and a screw speed of 80 rpm. Temperature during masterbatch preparation in different extrusion zones Z1, Z2, Z3, Z4, Z5, Z6, Z7, Z8, Z9 and die were 177, 172, 173, 188, 190, 197, 202, 211, 215 and 180 °C, respectively.

LLDPE-based nanocomposite films were prepared then using an extrusion blowing method. The masterbatch and LLDPE resin in the selected weight ratios (to incorporate 0, 1, 2.5, 5 and 10 wt% ZnO NPs) were mixed uniformly, and thereafter, the compounds were blown into a film through a single screw extruder (RCP- 0625 Microtruder; Randcastle Extrusion Systems, Inc., NJ, USA) with a screw diameter of 160 mm and a screw L/D ratio of 27/1 with 0.000034 m^3 volume. Neat LLDPE films were prepared following the similar steps except master batch step.

2.3. Determination of film properties and characterization

2.3.1. Film thickness

The thickness of films was measured using a digital hand-held micrometer (Mitutoyo, Model MCD-1“PXF, Mituyoto Corp., Kawasaki-shi, Japan) with an accuracy of 0.001 mm. Ten random locations around each film sample were used for thickness determination.

2.3.2. Mechanical properties

Tensile strength (TS) and elongation at break (EAB) of films were measured using a Texture Analyzer TA.XT plus (Stable Micro Systems, UK) with a 50 N load cell equipped with tensile grips (A/TG model) following the standard method D882 (ASTM, 2001). Grip separation was set at 50 mm and cross-head speed was 50 mm/min. TS and EAB were evaluated in ten samples from each type of film.

2.3.3. Rheological measurements

Melt rheology of films were measured using a Discovery Hybrid Rheometer HR-3 (TA Instruments, New Castle, DE, USA) attached with an electrically heated plate (EHP) at selected temperature (140, 150, 160 and 170 °C). Film samples were placed between the plates (measuring plate diameter 25 mm) in a 500-µm gap for 5 min so that the residual stresses would relax before rheological measurement. Frequency sweep tests (0.01–10 Hz) were carried out in the linear regime, at constant strain (0.01%) at selected temperatures. All rheological measurements were carried out in duplicate and rheological parameters were obtained directly from the manufacturer supplied computer software (TRIOS, TA Instruments, New Castle, DE, USA).

2.3.4. Colur, UV barrier and light transmittance of LLDPE nanocomposite films

Color of the films was determined using a CIE colorimeter (Hunter associates laboratory, Inc., Reston, VA, USA). Color of the film was expressed as L^* − (lightness), a^* − (redness/greenness) and b^*– (yellowness/blueness) values. Total difference in color (ΔE^*) was calculated according to the following equation (Gennadios, Weller, Hanna, & Froning, 1996):

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5}$$

where ΔL^*, Δa^* and Δb^* are the differences between the corresponding color parameter of the samples and that of white standard ($L^* = 93.56$, $a^* = -1.31$, $b^* = 0.23$).

The light transmittance of films was measured at the ultraviolet and visible range (200 nm–800 nm) using a UV–visible spectrophotometer (Shimadzu UV-1800, Kyoto, Japan) according to the method of Shiku et al. (2004).

2.3.5. Oxygen transmission rate

The oxygen transmission rate (OTR $cm^3\ m^{-2}\ 24\ h^{-1}$), was measured with an Extra-Solution PermeO$_2$ instrument, Capannori (LU), Italy at 25 °C and 50% RH on extruded LLDPE films through an area of 50 cm^2. Films were placed into the test cell and exposed to 98% N_2 + 2% H_2 flow on one side and pure oxygen flow on the other. Gas flow was regulated at 20 ml/min.

2.3.6. X-ray diffraction (XRD) analysis

X-ray diffraction analysis of the selected films was performed using a diffractometer Bruker D8 Advance (Bruker AXS, Germany) equipped with monochromatic Cu-Kα radiation (λ = 0.154 nm) under a voltage of 40 kV and a current of 40 mA. All samples were analyzed in continuous scan mode with the 2θ ranging from 5 to 70°.

2.3.7. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy

The FTIR spectra of film samples were determined using a Nicolet iS5 FT-IR Spectrometer (Thermo Scientific, Madison, WI, USA) over a wavelength range of 650–4000 cm^{-1} equipped with an OMNIC operating system software (Version 9.0, Thermo Scientific, Madison, WI, USA) to obtain FTIR spectra. Film samples were covered on the surface in contact with attenuated total reflectance (ATR) on a multi-bounce plate of Zn-Se crystal at 25 °C. All spectra were background corrected using an air spectrum, which was renewed after each scan. Each spectrum was collected from an average of 32 scans at a resolution of 4 cm^{-1} and the results were reported as mean values.

2.3.8. Differential scanning calorimetry (DSC)

Thermal properties of film samples were determined using a TA Q2000 differential scanning calorimeter (DSC) under a nitrogen atmosphere. Film samples (≈10 mg) were accurately weighed into aluminium pans, hermetically sealed, and scanned over the temperature range of −20 °C to 250 °C with a heating rate of 10 °C/ min. In the 1 st cycle, film samples were equilibrated at −20 °C and isothermed for 5 min; heat to 250 °C at 10 °C/ min and isothermed for 3 min; cool to −20 °C at 10 °C/ min. Similar steps were followed in the 2nd cycle. The empty aluminium pan was used as a reference.

2.3.9. Thermo-gravimetric analysis (TGA)

The thermal stability of the films (≈10 mg) was weighed into a platinum pan and were scanned using a thermo-gravimetric analyzer (TGA-7, Perkin Elmer, Norwalk, CT, USA) from 40 to 600 °C at a rate of 10 °C/min (Nuthong, Benjakul, & Prodpran, 2009). Nitrogen was used