Journal of Food Engineering xxx (2017) 1–11

Contents lists available at ScienceDirect

Journal of Food Engineering

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

Effects of metal nanoparticles on the physical and migration properties of low density polyethylene films

Süleyman Polat [a, *], Hasan Fenercioğlu [a], Mehmet Güçlü [b]

[a] Department of Food Engineering, Faculty of Agriculture, Cukurova University, Balcalı, 01330, Adana, Turkey
[b] Super Film Inc., Gaziantep, Turkey

ARTICLE INFO

Article history:
Available online xxx

Keywords:
Nanoparticles
Mechanical properties
Migration
Zinc oxide
Silver
LDPE

ABSTRACT

This paper reports the impact of the addition of Ag or ZnO nanoparticles on the morphological, mechanical, barrier properties and migration behavior of low-density polyethylene (LDPE) films prepared by melt extrusion. Depending on the nanoparticle concentrations, the color of the films was changed, and the light transparency decreased. The addition of nanoparticles reduced the oxygen and water vapor transmission rates, as well as the mechanical (tensile strength and percent elongation) properties, compared to pure LDPE films. ZnO nanoparticles caused a greater decrease in the tensile strength of the nanocomposite films than the Ag-containing nanoparticles. The migration tests of the majority of the films, in isooctane, ethanol and acetic acid showed that the total migration limit of 10 mg/dm^2 was not exceeded. However, the migration tests of LDPE-based films containing 3 and 5% ZnO nanoparticles in 3% acetic acid, representing acidic foods, were determined as 15.93 and 23.29 mg/dm^2, respectively.

1. Introduction

Low-density polyethylene (LDPE) films typically display good moisture barrier, low melting point, heat-sealable, chemically inert and color-free properties and shrinks when heated, but possess a relatively high gas permeability, oil sensitivity and poor odor resistance. They also maintain their physical properties up to −60 °C. Moreover, LDPE films are less expensive than most thermoplastic polymer films and, consequently, find extensive use in food packaging applications, including shrink or stretch wrapping and many types of bags and pouches. LDPE is used as an adhesive layer for multilayer composite structures, as a coating on paper to provide water protection (such as in milk cartons) and for various other purposes, such as flexible lids for plastic tubs and in squeezable plastic tubes and soft squeeze bottles (Robertson, 2016).

The use of nanotechnology in food packaging is considered to be highly promising because it has brought great opportunities for the development of materials with new properties. The inclusion of nanoparticles as the filler material in producing food packaging materials is known to improve packaging performances, such as gas, moisture, ultraviolet (UV) and volatile barrier attributes and mechanical strength, thereby extending the shelf-life of foods (Ayhan et al., 2015). Recently, inorganic materials, like metal and metal oxides, have been the focus of nanotechnology research, as they can be formed under conventional process conditions and demonstrate a high stability under extreme temperatures and pressures (Nafchi et al., 2012). In contrast, the sensitivity of organic materials to intense processing conditions restricts their usage in the food packaging industry. Thus, the interest in nano-sized inorganic compounds has been continuously increasing. Zinc oxide (ZnO) and silver (Ag) have received particular interest because their bulk forms are currently used industrially for several purposes (Gajjar et al., 2009).

Ag (in bulk form) is used to control bacterial growth in a variety of applications, including dental work, catheters and burn wounds (Kim et al., 2007) and it is also approved for use in food coloring in the European Union (EU). Additionally, Ag nanoparticles are used as a filler or cover for packaging material, primarily for their antimicrobial activity (de Azeredo, 2013; Emamifar et al., 2011). The food industry uses ZnO as a source of Zn, which is an essential micronutrient that serves important and critical roles in growth, development and well-being, in humans and animals (Shi et al., 2008). It is reported that ZnO has little toxicity in bulk size and it is widely used as an active ingredient for dermatological applications in sun creams, on account of its antibacterial and UV-blocking characteristics (Chee et al., 2012; Espitia et al., 2012; Li et al., 2009). In the

* Corresponding author. Department of Food Engineering, Faculty of Agriculture, Cukurova University, Balcalı, 01330, Adana, Turkey.
E-mail address: polats@cu.edu.tr (S. Polat).

https://doi.org/10.1016/j.jfoodeng.2017.12.004
0260-8774/

drug delivery and medical devices industry, ZnO is used for its strong antimicrobial effect on a broad spectrum of microorganisms (Zhang et al., 2011). In Europe, ZnO (in bulk form) is also authorized as an additive for plastic materials in contact with food.

The use of inorganic nanoparticles in nanocomposite packaging film production is a relatively new research area. Diverse methods exist to incorporate inorganic nanoparticles into various polymeric substrates. One conventional approach deposits metallic nanoparticles directly onto the surface of the material, for example, by vapor coating, sputter coating or ion beam coating. Another method of coating nanoparticles onto a substrate involves deposition or electrochemical deposition of nanoparticles from solution. Alternatively, melt blending is a conventional approach to obtain polymer composites, which incorporates nanoparticles into molten polymers (Duncan, 2011; Kumar and Munstedt, 2005). When comparing the production methods, the melt blending method is considered the easiest, cheapest and most effective for decreasing migration values.

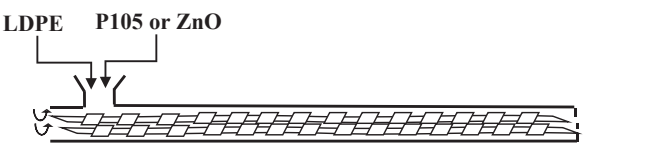
LDPE-based nanocomposite films that contain P105 (95% TiO_2 core coated with 5% Ag nanoparticles) or ZnO are already produced, and their potential use for orange juice packaging has been documented (Emamifar et al., 2010). However, there is no detailed information about that migration (total and specific migration values) and optical (color and light transmittance) properties of the films, which are important features in the food industry, and for thermoplastic film producers and researchers who are studying nanocomposite films. In this study, nanocomposite films were produced by adding P105 and ZnO nanoparticles, respectively, at four different ratios to LDPE polymer. The effects of the nanoparticles and their concentrations on the structural and physical properties of the films were investigated, and the migrations of Ag and Zn ions from the nanocomposite films were determined by the use of food simulants.

2. Materials and methods

LDPE pellets (MFI, 2.5 g/10 min; density, 0.918–0.922 g/mL) were supplied by Petkim (Turkey). ZnO nanoparticle powder, with an average particle diameter of 70 nm, and commercial Ag powder P105 (95% TiO_2 and 5% metal Ag nanoparticles of about 10 nm in diameter), were obtained from Pars Nanonasb (Persia). Chromatography grade ethanol, isooctane and acetic acid were purchased from Merck Co. (Germany).

2.1. Preparation of LDPE-based nanocomposite film

The nanocomposite films were prepared by the melt blending method. LDPE and LDPE-based nanocomposite films were prepared in two steps. First, LDPE was blended with P105 and ZnO nanoparticles, respectively, using a twin-screw extruder (Rondol Microlab, UK) with an $L/D = 40$ mm and $D = 21$ mm. The screw speed was set at 100 rpm, and the temperature profiles used in different areas of the twin-screw extruder are provided in Fig. 1. During the process, LDPE pellets and P105 or ZnO nanoparticles were fed through the main hopper of the extruder by feeders. The masterbatches, namely, 24% for P105 and 18% for ZnO, were produced by palletization and dried at 40 °C for 10 h. In the second step, the masterbatch pellets were diluted with neat LDPE pellets to obtain films with different metal nanoparticle contents. Then, the pellets were shaped as films by a single-screw extruder and blown film unit. The thermal profile of the extruder was 145, 155 and 150 °C and the screw speed was set at 100 rpm. The nanocomposite films were manufactured under the same conditions so that there would be no differences in the thermal history between them. The final P105 or ZnO contents were 0.5, 1.0, 3.0 and 5.0 wt% of the film, and correspondingly coded as PE(0.5Ag), PE(1Ag), PE(3Ag) and PE(5Ag) for those containing P105 and PE(0.5ZnO), PE(1ZnO), PE(3ZnO), PE(5ZnO) for those with ZnO, respectively. Also, plain LDPE films were coded as PE, and produced under the same process conditions, but without nanoparticle addition.



T_1(°C)	T_2(°C)	T_3(°C)	T_4(°C)	T_5(°C)	T_6(°C)	T_7(°C)	T_{DIE}(°C)
129	135	140	147	150	154	161	165

Fig. 1. Temperature profile in the different areas of the twin-screw extruder.

2.2. Color

Surface color of the films was measured using a CR-400 chromameter (Minolta Co., Osaka, Japan) with CIELAB scale and precalibration against a white ceramic tile. The total color difference (ΔE) was calculated as:

$$\Delta E = [(L^* - L^*_{\text{nanocomposite film}})^2 + (a^* - a^*_{\text{nanocomposite film}})^2 + (b^* - b^*_{\text{nanocomposite film}})^2]^{0.5} \quad (1)$$

where L^* (lightness), a^* (redness) and b^* (yellowness) are the mean color values of plain LDPE (control) films. Additionally, the hue angle (h°) and chroma (C^*) values were calculated as $h^\circ = \arctan b^*/a^*$ or 180 + arc (b^*/a^*) and by taking the square root of $a^{*2}+b^{*2}$, respectively.

2.3. UV light absorbance and light transmittance (%)

The UV light absorbance and transmittance of the film samples were measured by using a UV–Vis spectrophotometer (Lambda 35, Perkin Elmer, USA), according to Lahtinen et al. (2014) with a slight modification. The UV light absorbance was measured at 250, 280, 300, 315 and 340 nm, while the percentage light transmittance was measured over the range 400–700 nm.

2.4. Scanning electron microscopy (SEM)

The morphology of the LDPE-based films was examined using a scanning electron microscope (Zeiss Leo 1430 SEM, Oberkochen, Germany). Small sections (1 cm^2) were cut from the films, mounted onto aluminum stubs and coated under vacuum with a thin layer of gold/palladium.

2.5. Mechanical properties and infrared spectroscopy

For the determination of tensile strength (TS) and elongation at break (ε), the load-distance curves of each film were acquired and evaluated with a TA.XT Plus (Stable Micro Systems, Surrey, UK) instrument, using the ASTM Method D 882–12 (ASTM, 2012). Initial grip separation was set at 50 mm and cross-head speed at 50 mm/min with a 50-kg load cell. Tensile test specimens were prepared as 15-mm-width strips, according to ISO 1184, and the tests were carried out at 25 ± 2 °C and 52 ± 2% relative humidity (RH). The elastic modulus (E) values of the films were calculated from the slope of the stress-strain curves. Ten samples were tested for each film, and the mean values and standard deviations were reported.

Fourier transform infrared (FTIR) spectra of LDPE-based films were obtained using a Perkin Elmer 400 FT-IR/FT-NIR spectrometer

Please cite this article in press as: Polat, S., et al., Effects of metal nanoparticles on the physical and migration properties of low density polyethylene films, Journal of Food Engineering (2017), https://doi.org/10.1016/j.jfoodeng.2017.12.004