



Development of LLDPE based active nanocomposite films with nanoclays impregnated with volatile compounds

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ABSTRACT

In this study, a novel procedure was performed for grafting of nanoclays (montmorillonite (MMT) and halloysite (HNT)) with essential oil constituents (thymol (THY), eugenol (EUG) and carvacrol (CRV)) using Tween 80 as surfactant and then the nanoclay particles were incorporated into LLDPE pellets (5 wt%) to produce active nanocomposite films using a twin screw extruder. The resulting nanocomposite films were analyzed for antimicrobial and antioxidant capacity as well as thickness, mechanical, color, barrier, thermal properties and surface morphology and molecular composition. Release of the active compounds from the films at the refrigerated and room temperature conditions were also tested. The results showed that the films had strong in vitro antibacterial activity against pathogenic bacteria (*Salmonella* Typhimurium, *Escherichia coli* O157:H7, *Listeria monocytogenes*, *Staphylococcus aureus* and *Bacillus cereus*) while their effect against lactic acid bacteria (*Lactobacillus rhamnosus* and *Lb. casei*) was limited. The lowest and highest DPPH scavenging ability levels were 65.59% and % 87.92, belonged to THY-MMT and EUG-MMT, respectively. Release of active compounds at 24 °C was much more rapid than at 4 °C. CRV-HNT and THY-HNT provided slower release than the other films. SEM results showed that nanoclays were uniformly dispersed in the polymer matrix with exceptional agglomerates. Incorporation of the active nanoclays significantly ($P > 0.05$) improved tensile strength and elongation of the films. The results confirmed that LLDPE based active nanocomposite films could be successfully produced due to its good interaction with MMT and HNT, activated with THY, EUG and CRV.

1. Introduction

Food packaging is one of the major driving forces of food industry that is consistently gaining new concepts depending on consumer demands. Active packaging is defined as the incorporation of certain additives into packaging materials or into packaging containers in order to maintain/extend shelf life of packaged foods (Day, 2001). Antimicrobial packaging is a form of active packaging which can inactivate/inhibit undesirable microorganisms that may be present in the packaged food (Appendini & Hotchkiss, 2002). As a result of several reasons such as globalization and long transportation periods, increasing consumer demand for fresh and minimally processed foods, strict regulations related to food safety etc., antimicrobial food packaging has gained importance in recent years.

Antimicrobial agents can be applied in the packaging with different ways. Incorporation of antimicrobial agents directly into polymers is one of the most common types of antimicrobial packaging and has several commercial applications. However, direct incorporation of

antimicrobials into polymers has some drawbacks such as immiscibility of polymer and antimicrobial because of their hydrophobicity/hydrophilicity and rapid depletion of antimicrobials thereby short period antimicrobial effect (Appendini & Hotchkiss, 2002).

Nanotechnology presents outstanding opportunity in food technology area. Food packaging is one of the major applications of a nanotechnology with the economic magnitude of 4.13 billion USD in 2008 (Mihindukulasuriya & Lim, 2014). Nano-scale fillers such as nanoclays with different geometries has been demonstrated to improve material properties such as mechanical and barrier properties of bio-based and synthetic polymers (Abdollahi, Rezaei, & Farzi, 2012). Nanoclays are characterized with their high surface area giving them high surface activity. Montmorillonite (MMT) and halloysite (HNT) are nanoclays with platelet and tubular structure, respectively. Both clays have been extensively investigated in food packaging applications as nanofillers and carriers of active compounds. In this study, those nanoclays were grafted with active volatile compounds, namely thymol (THY), eugenol (EUG) and carvacrol (CRV) using a novel way of impregnation to

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produce active clay nanoparticles. Then linear low density polyethylene (LLDPE) based films were produced by incorporating with the active nanoclays using blown extrusion method. Therefore, this study was conducted to make characterization of the resulting active nanocomposite films impregnated with different active volatile compounds in terms of a series of characteristic properties.

2. Materials and methods

2.1. Film preparation

Linear low-density polyethylene (LLDPE, melt flow index 2000 g/10 min, density 0.918 g/cm³ at 23 °C, crystal melting point: 121 °C) was provided from Lotrene (Qatofin Company Ltd., Doha, Qatar). Na⁺ montmorillonite, (MMT, surface area 250 m²/g), halloysite, (HNT, surface area 64 m²/g, 30–70 nm × 1–3 mm nanotube), thymol (THY, 98% purity, vapor pressure 1 mm Hg at 64 °C) and carvacrol (CRV 98% purity) were purchased from Sigma (Germany). Eugenol (EUG, 99% purity) and nonionic Tween 80 (mol wt ~1310) was purchased from Merck (Germany).

Film manufacture procedures were specified in our previous paper (Tornuk, Hancer, Sagdic, & Yetim, 2015). Prior to film preparation, active compounds namely THY, CRV and EUG were impregnated to the nanoclays. For this purpose, 3 mL of active compound and Tween 80 were mixed in a beaker at room temperature. Distilled water (100 mL) was slowly incorporated with the active compound/surfactant mixture under continuous mixing for ~10 min. Then the nanoclay (3 g) was added into the mixture and mixing was proceeded for 3 h at ambient conditions. The precipitate was obtained by the centrifugation of the suspension at 5000 rpm for 5 min and dried at room temperature for 48 h. The nanoclay particles loaded with the active compounds were obtained by milling the dried nanoparticles using a ball mill (Fritsch™ Pulverisette 7 Premium Line, Germany).

Melt intercalation method was used for production of LLDPE based active nanocomposite films. A twin-screw extruder (L/D = 35, D = 16 mm, Gulnar Machines, Istanbul, Turkey) and a temperature profile of 40, 175, 180, 175 and 180 °C was employed for film production. Extrusion parameters such as feeding rate, temperature profile was optimized by preliminary works. The clay nanoparticles were incorporated with the LLDPE pellets (5 wt%) from the same feeding port. The active nanocomposite films were prepared as stated in Table 1. Control sample was prepared without incorporation of the active clay nanoparticles. In our preliminary studies, due to the poor antimicrobial/antioxidant activity of EUG grafted HNT nanoparticles, it was not used in nanocomposite film production as a nanofiller and thereby not listed in Table 1.

2.2. Scanning electron microscopy

Surface morphologies of the LLDPE based active nanocomposite films were analyzed by SEM (SEM LEO 440 Stereoscan). At least 10

Table 1
Active compound grafted nanocomposite film samples prepared by melt extrusion method.

Sample No	Film ID	Film information
1	Control	Neat LLDPE film
2	CRV-MMT	LLDPE film reinforced with carvacrol grafted montmorillonite
3	CRV-HNT	LLDPE film reinforced with carvacrol grafted halloysite
4	EUG-MMT	LLDPE film reinforced with eugenol grafted montmorillonite
5	THY-MMT	LLDPE film reinforced with thymol grafted montmorillonite
6	THY-HNT	LLDPE film reinforced with thymol grafted halloysite

images were obtained.

2.3. Fourier transform infrared (FTIR) spectroscopy

In order to make molecular characterization of the active nanocomposite films reinforced with the nanoclays grafted with THY, EUG or CRV, their FTIR spectra was analyzed by a FTIR tool (Perkin Elmer Spectrum 400, Perkin Elmer Instruments, USA). Measurements were performed at 450–4000 cm⁻¹ wavelength (Siripatrawan & Harte, 2010).

2.4. Thermal properties

Weight loss of the film samples during heating was analyzed by thermogravimetric analysis (TGA). In this process, the film samples were placed into the balance system and heated from 50 °C to 600 °C with a heating rate of 20 °C/min. The weight loss was measured as a function of temperature (Morawiec et al., 2005).

Thermal behavior of the active nanocomposite films were determined by differential scanning calorimetry (DSC, Model DSC-7, Perkin Elmer Instruments, USA). Five to ten milligrams of the film sample was placed into aluminum pans and heated from -10 °C to 160 °C. Melting temperature (T_m) and melting enthalpy (ΔH) were obtained. Crystallization level was calculated by the proportion between ΔH levels of the sample and 100% crystalline polyethylene (293 J/g). T_{95} and T_{50} values were also obtained in order to give information about thermal degradation of the samples.

2.5. Optical properties

Color properties (L^* , a^* and b^* values) of the LLDPE based active nanocomposite films were analyzed by a Hunter colorimeter (Lovibond RT Series Reflectance Tintometer, UK) (Rhim, Hong, Park, & Ng, 2006). Total color difference (ΔE) was calculated with the following formula:

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{0.5} \quad (1)$$

where $\Delta L = L_{standard} - L_{sample}$, $\Delta a = a_{standard} - a_{sample}$ and $\Delta b = b_{standard} - b_{sample}$ while standard values of the white plate were $L = 94.98$, $a = -1.04$ and $b = 0.55$.

Opacity values (%) of the film samples were determined by reflectance measurements according to Hunter lab method (Casariego et al., 2009).

2.6. Film thickness

Thickness of the active nanocomposite films reinforced with was measured using a digital micrometer (Fowler Digitrix Mark 2, Chicago, USA).

2.7. Oxygen permeability

Oxygen permeability (OP) of the active nanocomposite films was measured under controlled conditions (0% RH and 23 °C) based on the standard method of ASTM (2010) using an OxTran ST-2/21 modular system (Mocon Inc., Minneapolis, USA). The results were obtained as cc/m²·24 h taking account of the thickness values of the film samples.

2.8. Mechanical properties

Tensile strength (TS) and elongation at break (EB) values of the LLDPE based nanocomposite films were determined according to the standard method of ASTM (2012) using a texture analyzer (TA.XT Plus Stable Micro Systems, Surrey, UK) with a load cell of 5 kg. The film samples were cut in rectangular shapes (10 cm × 2 cm). The initial distance between the grips and crosshead speed were set to 50 mm and 4 mm/s, respectively. At least five replications were performed in order

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