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Preparation and antimicrobial properties of LDPE composite films melt-blended with polymerized urushiol powders (YPUOH) for packaging applications

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ABSTRACT

Polymerized solid-type urushiol (YPUOH) with high thermal stability and excellent antimicrobial properties was prepared and incorporated into low-density polyethylene (LDPE) via melt-compounding and subsequent melt-extrusion processes. To investigate the feasibility of as-prepared LDPE/YPUOH composite films for use in packaging applications, the films were characterized as a function of YPUOH using Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (WAXD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), contact angle, and antimicrobial activity assays. The physical properties and antimicrobial activities were found to be strongly dependent upon the changes in chemical and morphological structures originating from different compositions of the composite films. The thermal stability of the composite films was effectively improved with YPUOH addition. Incorporating YPUOH caused the water vapor transmission rate (WVTR) to decrease from 10.3 to 6.5 g/m^2·day, suggesting that the barrier properties of LDPE, which are relatively good per se, were further improved. Furthermore, the LDPE/YPUOH composite films exhibited good antimicrobial activities against both Gram-negative and Gram-positive micro-organisms. However, the dispersion of YPUOH in the LDPE matrix was not satisfactory due to a weak interaction between LDPE and YPUOH, which may adversely affect the thermal and barrier properties at higher contents of YPUOH. Further studies are required to increase the compatibility and dispersion of YPUOH in the LDPE matrix in order to optimize its performance and expand its applications.

1. Introduction

The primary purpose of food packaging is to protect and preserve foods from oxygen, water vapor, ultraviolet light, and both chemical and microbiological contamination [1–4]. Among all these modes of deterioration in quality, microbial spoilage and oxidative reactions have the greatest impact on reducing the shelf life of perishable foods [2]. Active food packaging systems are based on materials in which additives with antimicrobial and/or antioxidant properties are added into the polymer matrix with the aim of extending shelf-life and improving consumer safety.

Antimicrobial packaging can take several forms including addition of sachets containing volatile antimicrobial agents [5], incorporation of volatile and non-volatile antimicrobial agents directly into polymers [1–4], coating or adsorbing antimicrobials onto polymer surfaces [1], immobilization of antimicrobials to polymers by ion or covalent linkages [5], and use of antimicrobial polymers [5]. The food industry is increasing its focus on antimicrobial packaging materials and technologies due to the increasing consumer demands for minimally processed and preservative-free products [1–4].

The demand for the use of natural antimicrobial additives in recent years has led to a clear increase in the number of studies based on natural extracts for antimicrobial purposes. Additives such as essential oil, hinokitiol, and bamboo powder, which are categorized as Generally Recognized as Safe (GRAS) by the US Food and Drug Administration, are potential alternatives to synthetic additives like butylated hydroxytoluene (BHT) [1,3]. However, the choices of natural antimicrobial agents are often limited by their low thermal stability during high thermal and shear polymer processing, for example during extrusion and injection molding. In addition, natural antimicrobial materials are often incompatible

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with the polymer matrix [1,4,5]. It is especially desired for these natural antimicrobials to be compatible with the process of melt-compounding, the most straightforward and widely applied polymer processing technique [6,7].

Oriental lacquer is a natural antimicrobial material that has excellent barrier properties against oxygen and moisture, antioxidant and antimicrobial properties, salt resistance, heat resistance, insect repellent properties, and antiseptic effects [8–12]. It has been widely used in Asian countries for thousands of years as a medicinal plant, natural paint, and coating material. The sap from *Rhus vernicifera* sap comprises a latex material composed of 60–70% phenol derivatives (urushiol), approximately 20% water, plant gum including 5–7% saccharides, 2–5% water-insoluble glycoproteins, and 0.1% laccase enzyme. However, these lacquers are limited in commercial applications due to their high volatility, low drying rate, and allergenic properties. Due to poor safety and inconvenient handling characteristics, it is nearly impossible to melt-blend liquid-based urushiol with commodity plastics such as polyethylene and polypropylene. To overcome these limitations, polymerized powder-type urushiol powders (YPUOH), which are essential for convenient handling, have successfully been prepared through a random polymerization reaction of urushiol with a silane coupling agent [13,14]. YPUOH exhibits not only excellent antimicrobial activities against both Gram-positive bacteria and Gram-negative bacteria, but also antioxidant properties at least as strong as those of gallic acid and ascorbic acid [13,14]. Additionally, YPUOH showed relatively high thermal stability at temperatures greater than 250 °C, which makes it a good candidate for melt-extrusion or injection molding processes, which are commonly used for film formation in the industry.

In this study, six different low-density polyethylene (LDPE) and YPUOH (LDPE/YPUOH) composite films were prepared by melt-compounding LDPE with as-prepared solid-type YPUOH and subsequent melt-extrusion. The films were evaluated for applicability as active antimicrobial packaging materials as a function of YPUOH content. Lastly, the physical properties as well as their antimicrobial properties against various micro-organisms were assessed in light of their chemical structure and morphology.

2. Experimental

2.1. Materials

In this study, YPUOH powders were prepared using the random polymerization reaction of extracted urushiol (composition: 95% urushiol, 5% ethanol and laccase, Qingdao Xinyongan Industrial Co., Shandong, China) as the main raw material and 3-(trimethoxysilyl) propyl methacrylate (TPM, CAS No: 2530-85-0, Aldrich Chemical Co., USA) as a silane coupling agent according to our previous studies [13,14]. First, 50 g of urushiol and 150 g of hydrogen peroxide (CAS No: 7722-84-1, Daejung Chemical Co., Shiheung, Korea) were placed into a 500 ml flask equipped with a mechanical stirrer at 40 °C for 30 min. Next, 10 g of TPM was added to the mixture and stirred at 80 °C to initiate the reaction. After 2 h, solid-type YPUOH was obtained. To remove the unreacted reactants and solvent, YPUOH was filtered, washed twice with ethanol, and dried in a drying oven at 80 °C for 24 h. Finally, the as-prepared YPUOH mass was pulverized using an air jet-mill (Model: 04-626C-WC, Jet Pulverizer Co., Ltd., New Jersey, USA) to obtain fine YPUOH powders with average size of 14.6 μm.

The LDPE/YPUOH composite films were prepared by melt-compounding and melt-extruding as-prepared YPUOH and LDPE (Lutene LB7500, LG Chemical Co., Yeosu, Korea) to yield composite films with YPUOH loading contents of 0, 0.5, 1, 3, 5, and 10 wt%. Here, LDPE had a melt flow index (MFI) of 7.5 g/10 min (ASTM D1238) and a density of 0.918 g/cm^3. The LDPE/YPUOH composite films were processed with a laboratory-scale, twin-screw extruder (BA-19, BauTek Co., Uijeongbu, Korea) with a length/diameter (L/D) ratio of 40:19. Before melt-compounding and extruding, all ingredients were dried at 100 °C for 24 h to remove water. For melt-compounding the master batch of 10 wt% YPUOH and melt-extrusion of the composite films, the extruder was set to 170 °C for the header, 170 °C for zones 1–6, and 120 °C for the feed zone. The barrel pressures were 5.2 kg_f/cm^2 for the melt-compounding process and 4.65 kg_f/cm^2 for the extrusion process. The composite films were maintained at a thickness of approximately 70 μm to facilitate the evaluation of physical properties.

2.2. Characterization

2.2.1. Scanning electron microscopy (SEM)

To investigate the dispersion state of YPUOH in the LDPE matrix, SEM images for top and fractured surfaces of the LDPE/YPUOH composite films were obtained using a Quanta FEG250 scanning electron microscope (FEI Co., Ltd., Oregon, USA). To analyze the fractured surfaces of the LDPE/YPUOH composite films, the films were first frozen in liquid nitrogen and then shattered to produce a cross-section. Prior to examination, all samples were coated with a thin layer of platinum (Pt).

2.2.2. Wide-angle X-ray diffractometer (WAXD)

Morphologies of the composite films were assessed with a WAXD. WAXD patterns were collected on a D/MAX-2500H X-ray diffractometer (Rigaku Co., Ltd., Tokyo, Japan) with a nickel-filter and a CuKα (α = 1.5406 Å) radiation source. The radiation source was operated at 40 kV and 45 mA, and data were collected in the 2θ range from 2° to 80° at 0.02° intervals with a scan speed of 1.0°/min.

2.2.3. Fourier-transform infrared spectroscopy (FT-IR) and UV–visible spectra

To characterize the interaction between LDPE and YPUOH powders, FT-IR spectra were recorded on a Spectrum 65 FT-IR spectrometer (PerkinElmer Co., Ltd., Massachusetts, USA) from 400 to 4000 cm^{-1} in attenuated total reflection (ATR) mode. UV–visible spectra of the composite films were recorded with a single-beam OPTIZEN 2120 UV spectrometer (Mecasys Co., Daejeon, Korea) in the range of 200–800 nm, and a blank glass plate was employed as a reference.

2.2.4. Thermogravimetric analyzer

The thermal stability of the LDPE/YPUOH composite films was tested using a TGA 4000 thermogravimetric analyzer (PerkinElmer Co. Ltd., Massachusetts, USA) at a heating rate of 20 °C/min under a nitrogen atmosphere.

2.2.5. Water vapor transmission rate (WVTR)

The WVTRs of the LDPE/PW composite films were measured with a Permatran-W Model 3/33 water vapor permeation analyzer (Mocon Inc., Minnesota, USA) under 37.8 °C, 100% relative humidity, and a 10 cm^3/min nitrogen flow.

2.2.6. Antimicrobial activities

The antimicrobial activities of the LDPE/YPUOH composite films were investigated according to the JIS Z 2801:2000 standard. The microbes that were employed were strains DH5α *Escherichia coli* (*E. coli*) and KCCM 41665 *Vibrio vulnificus* (*V. vulnificus*) as target Gram-negative organisms and KCCM 11335 *Staphylococcus aureus* as a target Gram-positive organism. The *E. coli* and *V. vulnificus* were individually grown on a MacConkey agar plate, and *S. aureus* was grown on a trypticase soy agar plate at 38 °C for 24 h. A single colony was transferred into a 10 ml aliquot of nutrient broth or trypticase