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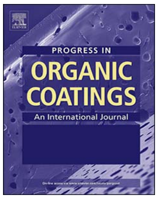

A pyrogallol-coated modified LDPE film as an oxygen scavenging film for active packaging materials

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ABSTRACT

Oxygen scavenging films were prepared with 1, 3, 5, 10, and 20% pyrogallol coated onto a modified LDPE film. The color, mechanical, barrier, and surface properties of the LDPE/PG oxygen scavenging films were compared to those of a pure LDPE film. The results demonstrate that pyrogallol was well coated onto the surface of the modified LDPE film. The LDPE/PG films had a slightly rough film surface, which results in higher water and oxygen permeabilities as well as lower TS due to the addition and agglomerations of sodium carbonate and pyrogallol. The pyrogallol coating also caused color alterations of the LDPE/PG film. In addition, the oxygen scavenging properties of the LDPE/PG films were evaluated at different relative humidities (RH) and temperatures. The oxygen content (%) in the headspace of the absorption cell containing the LDPE/PG 20% film, which was initially 20.9%, decreased to 9.42% after 8 days at 23 °C. The LDPE/PG 20% film showed an effective oxygen scavenging capacity of 0.443 mL/cm^2 at 23 °C. Water was used as an activator to initiate the oxygen scavenging reaction.

1. Introduction

Oxygen is a main cause of food spoilage. The amount of oxygen in the headspace of a package is responsible for oxidation in food products, resulting in changes of the flavor, color, texture, a loss of nutritive qualities, and hence, a shorter food shelf life [1–4]. To prevent such undesirable effects and to achieve a long food shelf life, the removal of oxygen and lowering the oxygen concentration from the package is a key target. Technologies including vacuum packaging (removal of gases), modified atmosphere packaging (MAP), and oxygen absorbing techniques have been used to reduce the concentration of oxygen from packages over the past two decades [5–7]. Among these technologies, vacuum technology and MAP are able to remove oxygen down to 1% in the package headspace during storage while on the other hand, an oxygen scavenger can reduce the oxygen concentration in a package to 0.01% [8]. An oxygen scavenger is able to absorb oxygen which diffuses through the wall of package from the outside environment into the package throughout the storage period and it also reduces the oxygen which is present inside the package before the sealing process [9]. Oxygen scavenging sachets, which contain iron (Fe)-based powder, are the most commonly used commercially established technology used to remove oxygen. However, oxygen scavenging sachets have several limitations for food packaging use. For example, there is the potential risk of accidental consumption by children and babies, packages containing oxygen scavenging sachets cannot be used in microwave ovens, and they create issues for metal detectors in the food production line. In addition, in the case of liquid food products such as juices, the use of oxygen scavenging sachets is not possible [10].

The use of organic-based oxygen scavenging materials has increased over the past few years in research studies involving organic-based products for active packaging use [11]. There are various ways to incorporate oxygen scavengers into polymers. Nevertheless, the choices for organic compounds are generally limited due to their low thermal properties in polymer processing such as polymer extrusion and injection molding processes [12,13]. Due to these reasons, the coating of oxygen scavenging compounds on the surface of a packaging material is a solution to overcome this issue.

For these reasons, researchers from the field of functional packaging have recently focused on non-metallic organic compounds as the main material for the development of oxygen scavengers [1]. Recently, several investigators developed oxygen scavenging films via a coating method [14–16]. These functional oxygen absorbing plastic films efficiently absorbed oxygen, which is important in food packaging.

Pyrogallol ($C_6H_6O_3$) (PG) is a natural phenolic compound found in different crops and fruits such as Litchi and Indian gooseberries [17]. It has been confirmed that some portion of pyrogallol is an active flavonoid constituent and presents a high oxygen absorbing activity since pyrogallol effectively reacts with oxygen [7]. It also has antimicrobial

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[18,19], antioxidant, antibacterial, and antiviral properties [20]. Pyrogallol is also an active ingredient employed in fruit storage [21] and is used in the development of active antimicrobial packaging materials [22]. Pyrogallol has a high oxygen scavenging ability in alkaline environments. Natural oxygen scavenging systems containing pyrogallol with sodium carbonate have high oxygen scavenging capacities and rates. As a result, they are used in food packaging applications [7]. The resulting solution when sodium carbonate (Na_2CO_3) is dissolved in water is alkaline and can be used as a catalyst in oxygen scavenging systems which contain pyrogallol as an active material.

In present study, a LDPE film was modified by blending with sodium carbonate and further coated with 1, 3, 5, 10, and 20% pyrogallol. The oxygen scavenging capability, rate of scavenging of the developed LDPE/PG film, and the influences of the storage conditions such as temperature and RH on the oxygen scavenging capacity of the LDPE/PG films were investigated. In addition to the scavenging activity, we also evaluated the surface morphology, chemical interaction, thermal, mechanical, barrier, and color properties of the resulting LDPE/PG films.

2. Materials and methods

2.1. Materials

Pyrogallol in powder form (anhydrous, 99%), sodium carbonate (anhydrous), and ethyl acetate were purchased from Daejung Chemical & Metal Co. Ltd (Jeongwang-Dong Siheung-Si Gyeonggi-Do, Korea). Polyurethane (HIPOL 859RT) was purchased from Hichem Co., Ltd. (Seoul, Korea). Aromatic polyisocyanate (KonnateL-75, 75%) as a hardener was purchased from Hanwha Fine Chemical (Yeosu-si, Jeollanam-do, Korea). LDPE resin (XJ700 LDPE) was purchased from LOTTE Chemicals (Yeosu, Korea). All chemicals were of reagent grade and used without additional purification.

2.2. Preparation of the modified LDPE films

A low-density polyethylene (LDPE) film was modified by incorporating sodium carbonate (SC). The modified LDPE films were prepared by using a laboratory scale twin-screw extruder (HEM, HANKOOK E.M Ltd., Gyeonggi-do, South Korea) with a length/diameter ratio of 40:19. All chemicals were of reagent grade and used without further purification. Before processing, all materials were dried at 80 °C for 24 h to remove moisture. Modified LDPE films with a sodium carbonate loading of 10% (w/w) were prepared. Before extrusion, sodium carbonate and LDPE resin were mixed by shaking in a glass jar. The temperatures of the extruder were set to 170 °C for the header zone, 170 °C for zones 1–6, and 120 °C for the feed zone. The barrel pressure was 5.3 kgf/cm^2 for melt-compounding and 4.61 kgf/cm^2 for the extrusion process.

2.3. Coating formation

The prepared modified LDPE films were further coated with pyrogallol. As presented in Table 1, different amounts of pyrogallol were slowly added to a 7 mL ethyl acetate solution followed by magnetic stirring to ensure that the pyrogallol particles were well dissolved in the ethyl acetate solution. Different amounts of polyurethane and hardener were added to the ethyl acetate solutions while stirring vigorously using an automatic stirrer for 30 min to produce the coating solution, followed by further stirring for 30 min. Then, each mixture was bar-coated onto a glass substrate containing a modified LDPE film sample (30 × 34 cm) using a plate stripe coater (PSC-300, PEMS., Yuseong-gu, Daejeon, 305–343, Korea), which was used to control the film thickness. The film thickness was maintained at about 61 ± 1 μm to aid in assessing the physical properties. The pyrogallol-coated films were dried at 45 °C for 24 h in a vacuum oven. Then, the prepared films were stored in a high barrier aluminum foil stand-up zip lock bag (9 × 17 cm) composed of PET/AL/PE (King Packaging Co., Ltd. Dongguan, Guangdong, China) until the experiments commenced. Finally, all of the film samples were studied to evaluate their physical, mechanical, and oxygen scavenging properties.

Table 1
Typical recipe of the PG/PU coatings with different amounts of PG.

Film Code	Pyrogallol (g)	Polyurethane (g)	Polyisocyanate (g)	Total amount (g)
LDPE/PG 1%	0.1	6.5	3.4	10
LDPE/PG 3%	0.3	6.3	3.4	10
LDPE/PG 5%	0.5	6.0	3.5	10
LDPE/PG 10%	1	5.5	3.5	10
LDPE/PG 20%	2	5.0	3.0	10

A control LDPE film without modification with sodium carbonate or a PG coating was developed using the same processing conditions and then placed in the same high barrier aluminum foil stand-up zip lock bag.

2.4. Properties of the prepared films

2.4.1. Color properties

The color properties of the LDPE/PG films were evaluated by using a Konica Minolta Chroma Meter (CR-300, Minolta Co. Ltd., Osaka, Japan). The L^* (lightness), a^* (redness), and b^* (yellowness) color values were measured. The total color change (ΔE^*) was calculated by employing Eq. (1) [2].

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

Here, $\Delta L = L_{standard} - L_{sample}$, $\Delta a = a_{standard} - a_{sample}$, and $\Delta b = b_{standard} - b_{sample}$.

2.4.2. Mechanical properties

The tensile strength (TS) and percent elongation (%E) of the prepared LDPE/PG films were analyzed by employing a universal testing machine (UTM, DaeKyung Tech & Testers Mfg. Co., Ltd., Namdong-ku, Incheon, South Korea) using a 50 kg load cell at a tensile velocity of 500 mm/min. The testing was performed per ASTM D882 [23]. All film samples were cut into 10 cm × 2.54 cm dimensions and then, the samples were conditioned in an atmosphere controlled chamber for 48 h at 23 °C and 50% RH. Five measurements were performed for each LDPE/PG film.

2.4.3. Thermal stabilities of the prepared films

The thermal stabilities of the LDPE/PG films were analyzed using a TGA 4000 thermogravimetric analyzer (PerkinElmer Co. Ltd., Waltham, MA, USA). The films were scanned from 20 to 700 °C at a rate of 20 °C/min. The melting temperature (T_m) of the films was measured by using a differential scanning calorimeter (2920 Modulated DSC, TA Instrument, Delaware, USA). The films were scanned from 30 to 400 °C at a rate of 10 °C/min. Nitrogen was employed as the purge gas at a flow rate of 20 mL/min in both the TGA and DSC analysis.

2.4.4. Fourier-transform infrared (FTIR) analysis

The infrared spectra of the prepared LDPE/PG films were obtained by using a FTIR-ATR spectrometer (1760X, PerkinElmer Life & Analytical Sciences, Inc., Waltham, MA, USA) to observe the structural interfaces of the pure and pyrogallol-coated LDPE films. Film spectra were recorded at a resolution of 16 cm^{-1} in the 4,000–450 cm^{-1} wavenumber range.

2.4.5. Determination of the film morphology

To examine the micro structure of the pyrogallol coating on the modified LDPE, SEM images of the top and fractured surfaces of the LDPE/PG films were analyzed by using a Quanta scanning electron