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Utilization of thymol as an antimicrobial agent for biodegradable poly(butylene succinate)

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HIGHLIGHTS

- PBS was softer and tougher due to the plasticization effect derived from thymol.
- OTR increased with increasing thymol due to the increased amorphous region.
- Thymol was found to effectively inhibit foodborne pathogens growth.
- Release kinetics showed that thymol was effective over 15 days studied.

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ABSTRACT

The poly(butylene succinate) (PBS)/thymol film was successfully prepared by using a blown film extruder at five different thymol concentrations ranging from 2 to 10 wt%. Experimental results indicated that PBS was softer and tougher due to the plasticization effect derived from thymol. The oxygen transmission rate (OTR) increased slightly with increasing thymol content due to the increased amorphous region in PBS structure. Under heating process, the blends exhibited lower crystallization temperature (T_c), enthalpy of crystallization (ΔH_c), enthalpy of melting (ΔH_m) and degree of crystallinity (X_c) than that observed in neat PBS. Thymol was found to effectively inhibit foodborne pathogens growth. Its antimicrobial activity against *Staphylococcus aureus* was evidence at 6 wt% while *Escherichia coli* did at 10 wt% thymol. Over 15 days studied, release of thymol showed some differences depend on food simulant. Maximum migration was obtained when the film was immersed in isooctane at all test duration. Release kinetics indicated that the incorporation of 10 wt% thymol to PBS films were effective over 15 days.

1. Introduction

Nowadays, food packaging is one of the major plastic wastes accumulating in the environment due to its non-biodegradabillity [1,2]. Major part of this waste comes from short-serviced life food such as dairy, meat and vegetable products. In recent years, the utilization of biodegradable polymers has drawn much attention from both industries and research institutions especially for non-durable applications [2–4]. Poly(butylene succinate) (PBS) is one of the biodegradable polymer derived from glucose fermentation and butanediol. Literature reviews indicated that PBS is one of a tough polymer with mechanical and thermal properties comparable to some petroleum based polymers [4]. Thus, PBS is possibly to be one of the commercial biopolymer in the near future.

During storage, some properties of food usually change due to the microbiological activity and others [2,5]. These changes allow further undesired deteriorations and consumer rejection [5–8]. To solve these problems, the preservatives have been applied to retard the food spoilage [9–11]. However, most of them affected the taste, the appearance or the odor of foods.

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In the past, the interaction between food and package was avoided due to its possibility of changing the food quality [5–8]. To date, it has been proved that some interactions do not affect the quality of food but capable to retard the food deterioration [6,7]. Antimicrobial packaging technology is one of the novel concepts which provide the interaction between food and packaging material while maintaining nutritional and sensorial qualities as well as safety [5–8]. This technology has drawn much attention from many researchers to produce polymer based antimicrobial packaging especially the use of bio-based essential oil and biopolymer.

Essential oil was initially used in Egypt, India and Persia more than 2000 years ago. Its antimicrobial inhibitory was discovered around a century ago [12]. Nowadays, many types of essential oils were used as antimicrobial agent in food packaging materials. The essential oil extracted from cinnamon was used as an antimicrobial agent in poly(ethylene terephthalate) (PET) film. It was found that the active PET showed the inhibition of *Aspergillus flavus* growth [13]. After incorporated to poly(lactic acid) (PLA)/poly(trimethylene carbonate) (PTMC) film, thymol was found to inhibit the growth of *Escherichia coli*, *Staphylococcus aureus*, *Listeria*, *Bacillus subtilis*, and *Salmonella* [14].

Thymol (2-isopropyl-5-methylphenol) is an essential oil extracted from thyme (*Thymus vulgaris*), onions (*Allium cepa*), garlic (*Allium sativum*) or other plants. It has been utilized as antimicrobial agent in polymer film due to its efficiency and physical properties suitable for blown film process. Numerous reports have found the potential of thymol when it was incorporated in polymer films. Rota et al. [15] concluded that thymol was an effective antimicrobial agent for preserving the food spoilage and increasing the shelf-life. Under microencapsulated condition, thymol showed significant inhibited the *Saccharomyces cerevisiae*, *Listeria innocua*, *E. coli* and *S. aureus* growths [16]. Although many literatures have reported the antimicrobial efficiency of thymol but no report exists in the PBS/thymol blends.

This study focuses on the development of PBS films with thymol. A blown film process was employed to produce the active PBS/thymol films. Evaluation of the *E. coli* and *S. aureus* inhibitory action was compared with various thymol concentrations ranging from 2 to 10 wt%. Other characterizations were carried out by determination tensile, thermal and oxygen barrier properties and release kinetics of the films.

2. Materials and methods

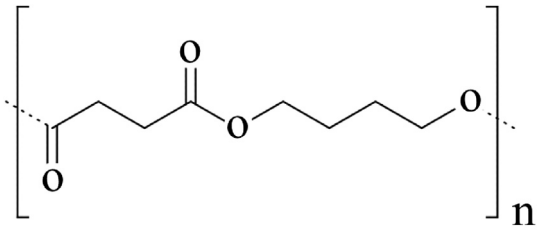
2.1. Materials and processing

A blown film grade PBS (FZ91PD) was used as a polymer matrix. Its melting temperature and melt flow rate were 110 °C and 6 g/10 min respectively. Thymol was selected as an antimicrobial agent to reduce the growth rate of *E. coli* and *S. aureus*. Fig. 1 illustrates the chemical structure of (a) PBS and (b) thymol.

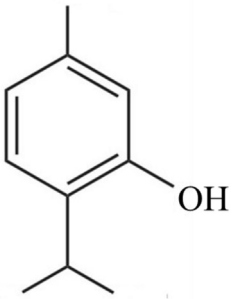
Formulations of PBS were prepared with various thymol concentrations of 2, 4, 6, 8 and 10 wt%. Thymol was firstly dry-blended with the PBS by using a high speed mixer (Thermo Prism Pilot 3) at 500 rpm for 30 s to disperse thymol powder in PBS matrix. The dry-blended compositions were then melt-blended by using a twin screw extruder (Labtech Engineering, LTE20-40). The barrel temperature was set at 100–150 °C and at the screw speed of 100 rpm. Each formulation was then pelletized and blown to obtain film of 100 μm in thickness for testing and characterizations.

2.2. Microorganisms

Microorganisms obtained from the culture collection of the Thailand Institute of Scientific and Technological Research (TISTR) included *E. coli* (TISTR 780) and *S. aureus* (TISTR 1466).



(a)



(b)

Fig. 1. Chemical structure of (a) PBS and (b) thymol.

2.3. Testing and characterizations

Tensile test was conducted by using a Universal testing machine (Instron 5567) equipped with a 1 kN load cell performed on rectangular films of 10 × 100 mm^2. Tensile modulus, tensile strength and tensile elongation at break were determined from the stress–strain curves according to ASTM D882. Test results were the average of five replicated specimens. A dart drop film impact test was conducted in accord with ASTM D 1709. An oxygen permeation tester (Mocon OX-TRAN, 2/21) was employed to measure the oxygen transmission rate (OTR) according to ASTM D 3985 with an oxygen flow rate of 40 cm^3/min at 23 °C and 0% relative humidity. To estimate the antimicrobial efficiency of thymol entrapped in PBS films, *E. coli* (gram-negative, TISTR 780) and *S. aureus* (gram-positive, TISTR 1466) were selected and measure the viability by using the agar diffusion method. The inhibition zone was determined after the PBS/thymol films were placed on the agar surface at 37 °C after 24 h incubation.

A differential scanning calorimeter (DSC) (PerkinElmer, DSC6000) was employed to evaluate the transition temperatures of PBS and PBS/thymol blends under nitrogen atmosphere. At the first heating step, the sample was heated from 30 to 150°C at a heating rate of 10 °C/min to remove the thermal history and followed by the isothermal holding at 150 °C for 10 min. The sample was then cooled from 150 to 30 °C at the identical heating rate. A second heating was then performed at the same conditions as the first heating. Finally, samples were cooled to room temperature. The degree of crystallinity (X_c) was calculated by using Equation (1) [17].

$$X_c = \frac{\Delta H_c}{\Delta H_f \times X_{PBS}} \times 100 \quad (1)$$

where ΔH_c and X_{PBS} are the crystallization enthalpy and mass