



# Release of thymol from poly(lactic acid)-based antimicrobial films containing kenaf fibres as natural filler



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## ABSTRACT

The migration of thymol, a natural antimicrobial (AM) substance, from poly(lactic acid) (PLA) films containing 300 g/kg kenaf fibres into food simulants is reported. Neat PLA and PLA/kenaf films containing 100 g/kg thymol were prepared *via* melt blending and heat pressing and were placed in contact with 150 mL/L and 950 mL/L ethanol/water mixtures at different temperatures. First-order kinetics, diffusion modelling and Fick's law modelling were used to describe the release. The release rate of thymol into 950 mL/L ethanol/water at different temperatures displays Fickian behavior with diffusion coefficient values between 1 and  $100 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  with close to 100% of thymol being released. The release rate of thymol is temperature dependent and is affected by the percentage of ethanol in the simulant. In the case of neat PLA and PLA/kenaf films, a faster release occurred in 950 mL/L ethanol/water than in 150 mL/L ethanol/water with the composite film exhibiting a higher diffusion coefficient in each case.

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## 1. Introduction

Controlled release systems in food packaging have experienced considerable growth recently due to developments in active packaging concepts such as the integration of antioxidant (AOX) and/or antimicrobial (AM) substances into packages in order to improve the quality and safety of food products. In these systems, low molecular mass compounds and/or substances are released from the package in a slow and controlled manner to maintain an adequate concentration of the substance in the packed food for a certain period of time. The release of substances that involve migration is the result of diffusion, dissolution and equilibrium processes (Crank, 1979). There are various factors that influence the migration of a substance from the packaging material including the film fabrication method, the volatility and polarity of the substance, the chemical interaction between the substance and polymer chains, hydrophobicity and hydrophilicity of the polymer as well as food properties and composition (Suppakul, Miltz, Sonneveld, & Bigger, 2003).

Poly(lactic acid) (PLA) is a polyester synthesized from the renewable, bio-derived, monomer lactic acid and can be used as AM

films and/or membranes for a different range of applications (Auras, Harte, & Selke, 2004; Karami, Rezaeian, Zahedi, & Abdollahi, 2013). This GRAS (Generally Recognized As Safe) grade polymer can be used in contact with food and fabricated *via* conventional processing procedures (Jamshidian, Tehrani, Imran, Jacquot, & Desobry, 2010). The use of fillers in combination with PLA has been widely studied with aims to improve physicomechanical properties, reduce production costs and enhance biodegradability. Naturally derived additives or fillers such as starch and cellulose can be combined with PLA and other active agents such as AM and AOX compounds. For example, Hwang *et al.* (2013) studied the migration of  $\alpha$ -tocopherol and resveratrol from poly(L-lactic acid) (PLLA)/starch blend films into ethanol and found that the neat PLLA containing  $\alpha$ -tocopherol had a lower release rate than the PLLA/starch blend films at 43 °C in 100% ethanol simulant with diffusivity coefficients of  $89 \times 10^{-11}$  and  $282 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$  respectively. A similar trend was observed for resveratrol, a non-volatile AOX compound with diffusion rate of  $25 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$  in neat PLLA and  $40 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$  in the PLA/starch films. Fortunati *et al.* (2012) prepared PLA AM films with 50 g/kg microcrystalline cellulose (MCC) and 10 g/kg silver nanoparticles by extrusion and injection molding techniques. The PLA films with silver nanoparticles and MCC had greater AM activity against *Escherichia coli* due to the presence of MCC; however, it had less AM activity than PLA films with silver nanoparticles. Although there are examples of

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the controlled release of AM and AOX substances from PLA materials (Busolo & Lagaron, 2013; Fernandez, Soriano, Hernandez-Munoz, & Gavara, 2010; Hwang et al., 2013; Iniguez-Franco et al., 2012; Llana-Ruiz-Cabello et al., 2015), few reports have combined PLA with natural fibres in order to control the release of active substances from composite films.

Antimicrobial packaging systems can be categorised as either migratory or non-migratory systems. In the former, AM substances migrate from the packaging material into the headspace of the package and onto the food surface, whereas in the latter, AM substances are immobilised onto the packaging material which is placed in direct contact with the foodstuff to facilitate its activity (Han, 2003). The integration of PLA with AM substances has been investigated by a number of researchers (Del Nobile et al., 2009; Jin, 2010; Qin et al., 2015; Rhim, Hong, & Ha, 2009). Of the reported studies, many have investigated the inhibition of targeted microorganisms with little attention having been devoted to studying the release rate from the active systems. This might be due to the preponderance of non-volatile and/or immobilised AM substances (e.g. nisin, chitosan, lysozyme and peptide) incorporated into PLA films rather than volatile AM substances (Green, Fulghum, & Nordhaus, 2011; Rhim, 2013; Tawakkal, Cran, Miltz, & Bigger, 2014b). Several AM substances have been incorporated directly into polymers including a range of volatile plant extracts such as basil, thymol, linalool, methyl cinnamate and cavacrol (Cran, Rupika, Sonneveld, Miltz, & Bigger, 2010; Del Nobile, Conte, Incoronato, & Panza, 2008; Fernández-Pan, Maté, Gardrat, & Coma, 2015; Rubilar et al., 2013; Suppakul, 2004; Suppakul, Sonneveld, Bigger, & Miltz, 2011; Tawakkal, Cran, & Bigger, 2015).

Thymol, an essential oil extract that has GRAS status, can be used in contact with food products and like other volatile AM substances, the migration of this substance into real food products is complex. In some studies, active AM films containing thymol were evaluated *in vitro* and *in vivo* against a wide spectrum of microorganisms such as bacteria, mould and yeast (Kuorwel, Cran, Sonneveld, Miltz, & Bigger, 2011; Wu et al., 2014). In a recent study by Petchwattana and Naknaen (2015), extruded films of poly(-butylene succinate) (PBS) containing thymol demonstrated AM activity against *E. coli* and *Staphylococcus*. Moreover, the release rate of thymol from the PBS films into 950 mL/L ethanol/water was found to be  $5.9 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ . Ramos, Beltrán, Peltzer, Valente, and Garrigós (2014a) reported that the migration of thymol from polypropylene (PP) films into 950 mL/L ethanol at 40 °C conformed to Fick's law with a diffusion coefficient of  $1.0 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ . In general, an AM substance can be released into a food simulant by swelling-controlled release with three main steps involved: (i) the absorption of fluid (penetrant) from the food simulant which leads to the swelling effect of the polymer, (ii) the active substance molecule being dissolved or dispersed in the polymeric matrix and (iii) the active substance migrating to the food simulant (Del Nobile & Conte, 2013).

The quantification of volatile AM substances in active films is an important consideration given that high pressure, shear forces and temperatures are required for film processing. According to Raouche, Mauricio-Iglesias, Peyron, Guillard, and Gontard (2011), a higher temperature of ca. 160–190 °C was needed to process PLA using extrusion which may easily degrade and evaporate the volatile AM substance during thermal processing. The retention of volatile additives such as thymol in PLA film was found to be approximately 70–80% after thermal fabrication (Tawakkal et al., 2015). Such retention percentages were significantly higher than those found in polyolefin film systems containing similar volatile additives. For example, Ramos, Jiménez, Peltzer, and Garrigós (2012) reported much lower retention of thymol and carvacrol (ca. 25–45% respectively) in PP formulations. The marked

reduction in the retention of these additives in polyolefin films upon thermal processing may result from the reduced compatibility between the polymer matrix and the natural additives as well as the processing parameters such as temperature, time and screw rotation (Del Nobile et al., 2009).

There are clearly many examples of the release of a wide range of AM substances from homopolymers such as PLA. However, little attention has been devoted to evaluating the release of AM agents from ternary composite systems, particularly taking into account the possible swelling of polymeric materials immersed in food simulants as well as the effects of natural fillers on the release rate. Moreover, the release of volatile AM substances from polymeric materials also has been restricted to mainly hydrophobic and moderate hydrophilic polymeric matrices (Buonocore, Del Nobile, Panizza, Corbo, & Nicolais, 2003; Herath, 2009). The aim of the current work was therefore to investigate the release of a naturally derived AM agent from a novel ternary system comprised of PLA, kenaf fibers and thymol. In particular, the release of thymol from PLA and PLA/kenaf composite and its diffusion kinetics were studied.

## 2. Experimental section

### 2.1. Materials

Poly(lactic acid) (7001D Ingeo™; specific gravity 1.24; melting temperature 152.5 °C (Tawakkal, Cran, & Bigger, 2014a)) was obtained from NatureWorks LLC, USA. Mechanically separated kenaf fibre (bast) was purchased from Ecofibre Industries, Australia. Thymol (T0501, purity of 99.5%) was purchased from Sigma Aldrich Pty. Ltd., Australia. Sodium hydroxide and acetic acid were purchased from Merck Chemicals, Australia. Un-denatured ethanol was purchased from Chem-Supply Pty Ltd., Australia. Isooctane (2,2,4-trimethylpentane, 36006) was purchased from Sigma Aldrich, Australia.

### 2.2. Production of PLA/kenaf/thymol films

Kenaf fibres were soaked in 0.05 g/mL sodium hydroxide for 2 h at room temperature. The fibres were then filtered and washed with distilled water prior to acid treatment to affect neutralization by adding a few drops of acetic acid. The fibres were then filtered, washed and rinsed with distilled water to remove the acetic acid, the latter being confirmed using a pH meter (inoLab® pH7110, WTW GmbH, Germany). Finally, the fibres were dried overnight in an oven at 105 °C. Prior to mixing, PLA resin and kenaf fibres were further dried in an oven at 60 °C overnight before mixing with thymol at 100 g/kg concentration.

The film samples were prepared firstly by melt-blending the components in an internal mixer (Haake PolyLab OS, Germany) at 155 °C for 8 min and 50 rpm followed by heat pressing, according to a method previously reported by Tawakkal, Cran, and Bigger (2014a). The PLA was added to the mixer first and the kenaf and thymol were introduced once the polymer was molten in order to avoid unnecessary loss of thymol. In the current study, a 300 g/kg loading of kenaf fibres was used to produce the PLA/kenaf composite that has moderate flexibility as well as high strength and stiffness compared with unfilled PLA which is more suitable for the production of rigid packaging applications (Tawakkal, Cran, & Bigger, 2014a). In a second step, a laboratory press (L0003, IDM Instrument Pty. Ltd., Australia) was used to prepare films. The samples were preheated at 150 °C for 3 min without applying pressure until the material melted, and then pressed at the same temperature for 2 min under a force of 20 kN before quench cooling to 30 °C under pressure. The average thicknesses of the pressed

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