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Morphological changes in multilayer polymeric films induced after microwave-assisted pasteurization

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ABSTRACT

In-package pasteurization of ready-to-eat (RTE) meals using microwave-assisted pasteurization system (MAPS) has shown promise for improving the safety and quality of foods, since dielectric heating is more efficient than thermal conduction. However, MAPS can affect the oxygen transmission rate (OTR) and water vapor transmission rates (WVTR) of packaging, imparting a certain degree of quality deterioration to the pasteurized food. This study evaluates morphological changes in newly-developed 3 multilayer polymeric films used for lidstock on trays subjected to MAPS. We measured changes in OTR and WVTR after MAPS treatment, and further correlated these measurements with melting enthalpy (ΔH), overall crystallinity, crystal structure, water absorption, and dielectric properties of films. The composition of tested films was: (Film A): polyethylene terephthalate (PET)/barrier PET/polyethylene (PE); (Film B): PET/Nylon-Polypropylene (PP) and (Film C): PET/low density polyethylene (LDPE)/Nylon/LDPE. Results show that the OTR and WVTR of the films significantly increased ($P < 0.05$) after both hot water and MAPS pasteurization. Films B and C exhibited a higher OTR after MAPS (52 mins) compared to hot water pasteurization (36 mins). The melting enthalpy (ΔH) of the films increased after pasteurization, and was correlated to the increase in overall crystallinity (1–4% increase) of the films. Increases in OTR and WVTR can be attributed to the fragmented crystal structures and smaller crystal size observed in *X*-ray diffraction. It is evident that the films absorbed water during MAPS, which altered their dielectric properties. In addition, it is likely that water absorption caused plasticization of the Nylon polymer, degrading the gas barrier properties of the film. Based on these findings, we recommend using a multilayer film with PET as barrier layer for MAPS treatment.

Industrial relevance: Commercialization of novel microwave-assisted thermal pasteurization technology will require development of multilayer films which can sustain microwave and thermal stresses. Food processes influence oxygen and water vapor barrier properties of films which may affect the shelf-life of food sensitive to oxygen and water vapor. A better understanding of the influence of microwave-assisted thermal pasteurization process on film properties will help polymer industry in the design and development of improved film structures.

1. Introduction

Pasteurization involves processing foods at temperatures of 70 to 90 °C to inactivate vegetative bacterial cells and viruses of public health significance (Peng, Tang, Barrett, Sablani, & Powers, 2014). Thermally pasteurized food retains higher sensory and nutritional quality compared to sterilized foods. Pasteurized foods have a shelf life of several days to few weeks at refrigerated temperature. Conventional hot water and steam-based thermal processes result in a certain degree of quality degradation for prepared meals. Microwave heating has the potential to deliver superior quality processed food. This is because volumetric heating works more efficiently. The microwave-assisted thermal pasteurization system (MAPS), based on a single mode 915 MHz with surface water heating, was developed at Washington State University to produce pre-packaged high quality refrigerated food (Tang, 2015).

MAPS requires in-package food and the packaging must be transparent to microwave radiation. Metal-based packaging is not suitable, since it blocks microwave radiation. Although polymeric-based packaging is suitable for MAPS, the packaging must maintain its visual appearance and integrity after processing. Little research has examined the influence of thermal pasteurization (Halim, Pascall, Lee, & Finnigan, 2009), microwave- assisted thermal sterilization (MATS) (Dhawan et al., 2014a; Mokwena, Tang, Dunne, Yang, & Chow, 2009), or pressure-assisted thermal sterilization (PATS) (Dhawan et al., 2014b) on the barrier properties of polymeric films. Dhawan et al. (2014a) reported a reduction in gas barrier properties of PET-based multilayer films. They demonstrated that retort sterilization had more influence compared to MATS processing due to longer processing times associated with retort

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processing. They correlated an increase in oxygen transmission rate with changes in crystallinity and free volume properties of the polymeric films. Mokwena et al. (2009) also reported that retort sterilization had more effect on the gas barrier properties of EVOH-based multilayer polymeric films than MATS processing. Deterioration in gas-barrier properties was attributed to the plasticization of the hydrophilic EVOH layer. Changes in gas barrier properties were often related to alteration in morphology of films; specifically, the crystalline structure, the proportion of crystalline and amorphous phase in the polymer, and free volume. Changes in oxygen and water vapor transmission rates were also related to melting enthalpy, and the melting peak of crystalline structure of semi-crystalline polymer using differential scanning calorimetry (DSC) (Halim et al., 2009; Kong & Hay, 2003). *X*-ray diffraction can further explain the morphological changes by calculating crystalline percentage in polymers (Yoo, Lee, Holloman, & Pascall, 2009). The higher the crystalline percentage, the greater the gas barrier properties and mechanical strength of polymeric films.

An understanding of morphological and gas barrier properties changes is required to design and develop multilayer film for microwave-assisted pasteurization process. This is the first study to determine changes in the morphology and barrier properties of multilayer films after microwave-assisted pasteurization treatment. The objective of this study is to investigate the influence of MAPS on gas barrier properties of three multilayer polymeric films. This study also examines post-pasteurization changes in terms of crystalline percentage, thermal and dielectric properties of polymeric packaging films and correlated to gas barrier properties.

2. Materials and methods

2.1. Multilayer polymeric films and rigid trays

Three multilayer polymeric films (A, B, and C) were selected as the lid film for this study. Film A had a structure of barrier layer of polyethylene terephthalate (PET), sandwiched between an outer layer of PET and an inner sealant layer of linear low density polyethylene (LLDPE), denoted as PET/barrier PET/tie/PE, with overall thickness of 88 μm. Film B consisted of an outer layer of PET and an inner layer of nylon 6 and polypropylene (PP) blend (PET/tie/Nylon 6-PP), with a total thickness of 104 μm. Film C was a coextruded structure with an outer layer of PET, a barrier layer of nylon 66, and an inner sealant layer of LDPE, denoted as PET/LLDPE/LDPE/tie/Nylon 66/tie/LLDPE/LDPE (thickness = 105 μm).

Rigid polymeric trays with a 10.5 oz (300 g) capacity (Silgan Plastics, Chesterfield, MO, U.S.A.) were selected for the packaging containers. The tray had the following structure: PP/regrind/tie/EVOH/tie/regrind/PP with total wall thickness of 1.1 mm, with an inner dimension of 14.0 cm × 9.5 cm × 3.0 cm.

2.2. Preparation of mashed potato

Mashed potato was prepared by mixing 15% (w/w) potato flakes (Oregon Potato Company, Pasco, WA) with preheated 84.5% (w/w) de-ionized water (80 ± 1 °C) and 0.5% (w/w) salt (Mokwena et al., 2009). The mixture was then cooled to ambient temperature (23 °C). Approximately 290 ± 1 g of mashed potato was filled into the rigid trays. The trays were then vacuum-sealed (400 mbar) with lid films (sealing conditions: 185 °C for 4 s dwell time) with a vacuum sealer (MULTIVAC T-200, Multivac Inc., Kansas City, MO, U.S.A.).

2.3. MAPS and hot water pasteurization processes

Pasteurization was carried out in a pilot scale 915-MHz, single mode, semi-continuous microwave assisted pasteurization system (MAPS) developed at Washington State University, Pullman, Washington. The system has four sections to simulate industrial processes, namely, preheating, MW heating, holding, and cooling. All sections were filled with water at controlled temperatures. A rigid metal carrier frame with a microwave transparent mesh was used to hold and transport the sealed trays through the cavities. The trays were loaded at the preheating section, which was maintained at 61 °C by hot water. The preheating section helps food to achieve a uniform initial temperature. After preheating, the trays were navigated through MW heating cavity. There, the foods were heated by MW energy and hot water maintained at 93 °C. The MW heating was followed by hot water heating (holding section) for product to reach 90 °C. Finally, all trays were cooled in the cooling section using tap water (23 °C). The process was designed to achieve a desired pasteurization value ($P^{7}_{90^{\circ}C} = 10$ min) for a 6 log reduction of psychrotrophic non-proteolytic *Clostridium botulinum* type E (ECFF, 2006) at cold spot in mashed potato. The time-temperature data of the cold spot of the trays were obtained using Ellab sensors (Ellab, Centennial, CO). Typical MAPS treatment of mashed potato involved preheating trays up to the temperature 61 °C for 30 mins, heating in the microwave section for 2 mins, hot water heating at 93 °C for 20 mins, followed by cooling for 5 min (Fig. 1). Thus, the overall processing time for MAPS would be 52 min (only heating time considered).

For conventional hot water pasteurization, the sealed trays were immersed in hot water in a steam-jacketed kettle, and the water temperature was maintained at 93 °C. The temperature of the cold spot was monitored by a T-type thermocouple (TMQSS-032U-6, 0.032-in. outer diameter, 6-in.-long, Omega Engineering, Stamford, Connecticut, U.S.A.). The time-temperature data (n = 2) were recorded at the cold spot in the mashed potato by a mobile data logger system (USB-TC, Measurement Computing, Norton, Massachusetts, U.S.A.).

The pasteurization value for both MAPS and hot water pasteurization was calculated using the general formula (Eq. (1)):

$$P^{z}_{T_{ref}} = \int_0^t 10^{\left(T(t)-T_{ref}\right)/z} dt \quad (1)$$

where $T(t)$ is the temperature of the cold spot, T_{ref} is the reference temperature, and the z value of the psychrotrophic non-proteolytic *C. botulinum* is 7 °C (ECFF, 2006). The overall exposure time for conventional hot water pasteurization to achieve $P^{7}_{90^{\circ}C} = 10$ min was approximately 36 min for all trays studied (Fig. 1). After pasteurization, the trays were rapidly cooled using tap water (23 °C). The lid films were carefully peeled from trays, wiped with dry paper and stored in glass vessels at room temperature (23 °C).

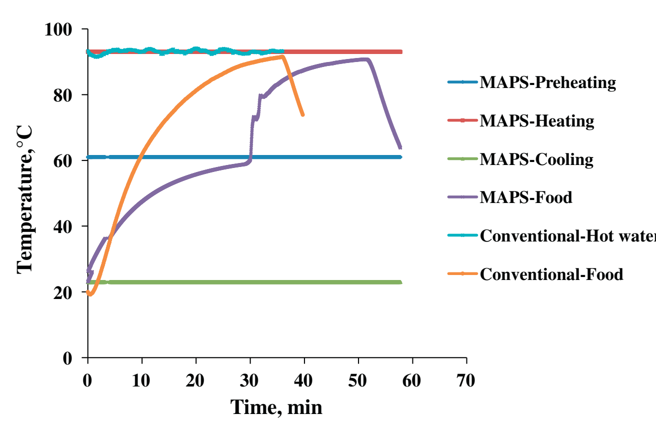

Fig. 1. Time-temperature profile of slowest heating region inside packaged mashed potato in a 10-oz tray during pasteurization.