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Effect of high-pressure processing on the migration of antioxidant Irganox 1076 from polypropylene film into a food simulant

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Abstract: The effect of high-pressure processing (HPP) on the migration behaviour of a typical antioxidant, Irganox 1076, from polypropylene (PP) flexible structures was studied. Initial concentrations of Irganox 1076 in polypropylene (PP) were 2.0 and 5.0 mg g^{-1}. The migration experiments were carried out on high-pressure treated and non-treated polypropylene pouches containing either 95 or 10% ethanol aqueous food simulating liquids (FSL) for 20 days at 40 and 60 °C. After the contact period, concentrations of Irganox in PP and FSL were measured to determine migration behaviour. The results showed that there was no significant difference in the concentration of Irganox 1076 migrating from PP, and into the FSL for pressure-treated vs non-treated samples. No significant concentration differences were found in non-treated (control) samples and those treated for 5 and 10 min. However, there was a storage time effect on the migration level. There was also a significant migration effect on the migration of Irganox between the two different food simulants, and an increase in the HPP temperature increased the rate of migration.

Keywords: high pressure; migration; antioxidant; polypropylene; food–package interaction

INTRODUCTION

High-pressure processing (HPP) is growing in interest as a food preservation method. Application of high pressure as a non-thermal preservation technology is being investigated as an alternative or complementary process to heat treatments. The technological development of HPP requires research on the effects of such treatment on the packaging material as well as on the food. Treatment of prepackaged foodstuffs with HPP helps reduce microbial contamination. However, a crucial question concerns possible effects of HPP on plastic packaging materials, and thus the quality and safety of the packaged foods. Appropriate food packaging is a critical element in assuring food quality and safety, and in preventing or reducing food losses.[1–3]

The increasing use of plastic structures in food packaging has lead to increased interest in the area of mass transport. Polymeric materials are not totally inert in direct contact with packaged food products. Food packaging interactions include transport of gases, vapours, water or other low molecular weight compounds, and also include chemical changes in the food, the package, or both.[4,5]

Three main kinds of interaction may take place at the interface between food and packaging: (i) permeation (oxygen, odours, moisture); (ii) sorption (aroma loss); and (iii) migration (additives, odour).[6,7]

Migration results in mass transfer of an additive from the package material to the food. This transfer may increase the risk of chemical hazards and/or formation of off-flavours. Any substance which migrates from the package material into the food is of concern if it could be harmful to the consumer. Even if the migrating substance is not potentially harmful, it could have an adverse effect on the flavour and acceptability of the food. The quality and ultimately the safety of packaged foods can be compromised by migration of chemicals from polymers. Consequently, additives in packaging materials must be safe, suitable for their purposes and adhere to requirements limiting migration of packaging material to foods.[8,9]

Flexible plastic structures often contain functional additives or processing aids, such as catalysts, antioxidants, heat stabilizers, plasticizers and colourants, which help to extend the usefulness of the plastic. Most of these additives are used in small amounts of no more than 1–2%. Polymeric structures are susceptible to oxidation and this oxidation leads to increased brittleness and deterioration in strength.[10,11] Polymeric films containing antioxidants protect against the oxidative

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deterioration of food products by providing a functional barrier to oxygen and/or inhibiting autoxidation of the product. To minimize the effects of oxidative degradation, antioxidants are often incorporated into polymers at concentrations of 0.001–1.0 wt%. Antioxidants are also added to polymers used for long-term application and/or when it is desirable to protect the polymer against thermal deterioration.[4,12]

Phenolic compounds such as BHT and Irganox are often used as antioxidants. These low molecular weight components can migrate into foods. For the packaging of foods, only those polymers should be used which contain mobile components in amounts that present no risk to consumers.[13,14]

Migration of antioxidants from polymers into foodstuffs is influenced by material properties. Foods are classified as aqueous, acidic, alcoholic or fatty since these characteristics are understood to influence the migration of organic and inorganic substances that may be present in packaging structures. Selection of the food simulant may influence the migration process. Simulants are substances that exhibit behavior similar to that of foodstuffs with respect to solutes.[15]

Food manufacturers that use HPP technology need to ensure the quality and safety of their food products. An understanding of mass transfer issues within the food/package system is important to ensure consumer confidence. Transfer of undesirable substances may result in organoleptic changes, product quality loss and concomitant reduction in shelf life, in addition to potentially creating a safety concern. Polymer components that migrate into food must be safe for human consumption. Interactions that occur between packaging structures and foodstuffs may restrict the use of polymer materials in certain food packaging applications.

While the microbiological and nutritional impacts of HPP-treated food have been studied in depth, there have been few investigations dealing with the effect of HPP on the migration behaviour of additives present in polymeric structures. Interaction between the food and packaging after HPP has not been fully defined. To date, only a few studies have been carried out in this area.

In this study, major objectives were to determine the effect of HPP on migration of the Irganox from PP film to food-simulating liquids (FSL). Variables studied included Irganox level, temperature, food simulant and time of exposure. The migration process was monitored as a function of storage time. Results were compared with migration rates for untreated packages.

MATERIALS, METHODS AND PROCEDURES

Food simulants

FSL included 95% ethanol, which was used to simulate both fatty foods and alcoholic foods (reagent HPLC grade, Sigma Chemical, St Louis, MO, USA); 10% ethanol was used as a simulant for acid foods.

Polypropylene resin

Polypropylene (PP) resin with controlled amounts of antioxidant, Irganox 1076 (Ciba, Tarrytown, NY, USA), was mixed and blended for 20 min using a Hobart Mixer Model K5SS (Troy, OH, USA). The mixed PP resin was extruded using a co-rotating twin-screw extruder (Baker Perkins Model ZSK-30 Werner & Pfleiderer Corporation, Ramsey, NJ, USA). Before blending, the extruder was purged for about 15 min using pure PP resin. Extruder conditions were 150 °C for ports 1 and 2 and 180 °C for ports 3–6. The extruder screw speed was 400 rpm (675 psi), and the feeder screw speed was 975 rpm. Virgin PP resin was provided by Exxon–Mobil Chemical. The initial concentration targets for Irganox 1076 in PP were approximately 2.0 and 5.0 mg g^{-1}.

Polypropylene film production

The PP films were fabricated on a 2.54 cm laboratory scale single screw Killion extruder interfaced with a bottom-fed blown film die (Davis-Standard Co., Cedar Grove, NJ, USA). The blended resins were processed at a constant screw speed of 8 rpm and 690 psi pressure. The extruder conditions were 445 F for zone 1, 2 and 3 and 415 F for die 1 and 2.

EQUIPMENT

High-pressure processing

High-pressure processing was carried out using a pilot scale QFP-6 Tetra-Laval Quintal high-pressure processor (ABB Autoclave System, Columbus, OH, USA). This equipment had a cylindrical 1 l processing vessel with an internal diameter of 6.0 cm and a height of 18.8 cm. It was designed for a maximum pressure of 890 MPa and an operational temperature range of 5–70 °C. The processing temperature was brought up to either 40 ± 2 or 60 ± 2 °C for each test run. The temperature increment produced by pressurization was considered in setting up the process conditions. For a typical 10 min HPP, three pouches were loaded into the pressure vessel which was preheated to around 30 °C. The chamber was sealed, then pressurized for 10 min (holding time) up to 800 MPa at 60 °C. The desired pressure was reached in 2.3 ± 0.25 min. A cooling system maintained the temperature of the chamber during the pressurization time. The high-pressure transmission fluid used in this equipment was Houghton-Safe 620-TY a glycol/water compound from Houghton International (Valley Forge, PA, USA).

HPP was carried out for 5 or 10 min at temperatures of 40 or 60 °C at 800 MPa. Taking into consideration the initial time of 2.3 min to come to full pressure, actual times for each temperature were 7.3 min for the 5 min trials and 12.3 min for the 10 min trials.

High-performance liquid chromatography

Quantification of the antioxidant Irganox 1076 was carried out using a reverse-phase high-performance

liquid chromatography (HPLC) method. Three replicate measurements for each data point with triplicate measurement were carried out. The HPLC system consisted of a Waters Model 150-C ALC/GPC and a Waters 486 Tunable Absorbance Detector interfaced to a Waters 730 Date Module for quantification (Waters Corporation, Milford, MA, USA).

An Irganox 1076 calibration curve was constructed to determine the relationship between standard area response and quantity injected. The chromatographic conditions were as follows: Column, Delta Pak™, C_{18}, 300Δ, 3.9 × 150 mm, Part no. 35571 (Waters Corporation, Milford, MA, USA); solvent system, 100% methanol; flow rate, 1.0 ml min^{-1}; detector wavelength, 280 nm; injection, 20 µl volume by automatic sample injection system with a loading capacity of sixteen 4 ml clear glass vials with screw tops (Supelco, Bellefonte, PA, USA) and PTFE Septum (Waters, Milford, MA, USA). Peak area and retention times were determined using a computing integrator with the following conditions: peak width, 20; noise reduction, 10. Quantitative analysis was done using an external standard calibration method (the retention time and area response were compared with a known concentration of Irganox 1076).

Sealing and processing pouches

Filled pouches were heat-sealed without headspace using a Sencorp heat-sealer (Sencorp Systems Inc., Hyannis, MA, USA). Samples were divided into two sets: one to be held at atmospheric pressure as control at 23 °C, and the other processed at high pressure. Control pouches were exposed to atmospheric pressure (1 atm) at 60 °C for 10 min in an electric oven. Additional control pouches were held at 1 atm at 40 °C for 10 min in an electric oven.

Storage

For each of the two FSL used, 12 PP pouches of nominally 2.0 mg g^{-1} Irganox 1076 were HPP processed at 60 °C for 10 min. Twelve pouches of nominally 4.0 mg g^{-1} Irganox 1076 were HPP processed at 40 °C for 10 min.

Twelve PP pouches of nominally 2.0 mg g^{-1} Irganox 1076 were HPP processed at 60 °C for 5 min. Twelve pouches of nominally 5.0 mg g^{-1} Irganox 1076 were HPP processed at 40 °C for 5 min.

A total of 96 PP pouches were HPP processed as control for each FSL, twelve pouches were held at 60 °C for 10 min at 1 atm. Twelve more control pouches were held at 40 °C for 10 min at 1 atm. Similarly, 12 pouches were held at 60 °C at 1 atm for 5 min and 12 were held at 40 °C at 1 atm for 5 min.

A total of 96 pouches were produced as control samples. Following processing, whether at HP or 1 atm, all samples were stored at 23 °C for a maximum time of 20 days.

Samples were removed for determination of Irganox 1076 in the PP and FSL using HPLC at 1, 3, 8 and 20 days of storage.

Sampling

Immediately after high-pressure processing, the PP materials and food simulants were analysed for Irganox 1076. Migration amounts were determined to 20 days' storage to provide sufficient information for statistically valid measurement of migration rates. This procedure was followed for both treated and untreated (control) pouches.

Evaluating migration: initial concentration in the polypropylene

To determine the initial concentration of Irganox 1076 in the PP samples, a soxhlet extraction method was used. For soxhlet extraction, known amounts of film (300 mg) were cut into small pieces and extracted with 150 ml of acetonitrile in a soxhlet extraction apparatus for more than 12 h. The extracts were filtered through an HV filter and analysed using HPLC. A second extraction was carried out to ensure complete extraction of antioxidant in the film. The second extraction contained less than 5% of the total antioxidant.

Antioxidant levels in the FSL were also measured as a function of time. Food simulants were transferred to glass vials and then capped using a polypropylene sampling cap with a PTFEE/silicone septa (Supelco, PA, USA). Level of antioxidant in the food simulants was determined using HPLC. The HPLC conditions were the same as described for the calibration curve.

Calculations

The level of Irganox 1076 in the film samples was calculated using the following equation:

$$Z = \frac{(Rs)(CF)(Vt)100}{(Vi)(Wp)}$$

where, Z = percentage of Irganox 1076 in polymer, wt wt^{-1}; Rs = HPLC detector area response, AU; Vt = total volume of solution, ml; Vi = volume of unknown injected solution, ml; CF = calibration factor, g AU^{-1}; and Wp = polymer weight, g.

Statistical analysis

Research was carried out to evaluate the combined migration effects of pressure (800 MPa), holding times (5 and 10 min) and holding temperatures (40 and 60 °C) on migration of Irganox (2.0 and 5.0 mg g^{-1}) as applied to PP pouches containing FSL (95% ethanol or 10% ethanol) during storage time. Irganox values were obtained from three replicate of each film sample. Each replicate was analysed twice. The control groups were prepared under normal atmospheric conditions; statistical analysis of the data was carried out using a mixed model procedure in SAS (SAS Institute Inc.).[16] Data were analysed using a lease-square means linear model. The model assumed a fixed relationship between factors, and pair-wise differences between combinations of factors. Statistical significance was defined as $p < 0.05$.

RESULTS AND DISCUSSION

Analysis of Irganox 1076 in PP and FSL

The average recovery of Irganox 1076 at first extraction was 92.1 ± 4%. These data demonstrate satisfactory recoveries for the first extraction and the stability of the additives under the extraction conditions used.

The results of quantitative analyses of Irganox 1076 in PP and in FSL after HP treatment are shown Figs 1–6. Irganox 1076 plots in 10% ethanol are not included because they were near or below the detection limits of the analysis method. No significant differences were observed in the concentration of Irganox 1076 in PP, or in the different FSL after HPP treatment vs the control samples.

However, significant differences were found in the migration of Irganox 1076 in PP depending upon the food simulant used. Migration into 95% ethanol was significantly higher than those for 10% ethanol. The cause of this difference is probably greater compatibility between PP and 95% ethanol. The larger migration values obtained for the 95% ethanol are due to the greater solubility of Irganox 1076 in the FSL and, consequently, a lower partition coefficient. These effects resulted in faster migration and more migration. During the first week of storage (23 °C), after HPP, the migration of Irganox 1076 was at a rate which brought the concentration in the FSL close to equilibrium.

Consequently, during simulated storage, migration of Irganox 1076 did not progress much further than its value at 20 days. PP film in contact with 95% v/v ethanol showed a rapid decrease in Irganox. In addition, the Irganox concentration in the FSL showed a correspondingly rapid increase. The loss of Irganox from the PP film can thus be assumed to be largely due to migration into the ethanol.

On the other hand, the migration of Irganox 1076 into 10% ethanol was significantly less rapid than the migration of Irganox into 95% ethanol for the polymers containing different concentrations of antioxidant.

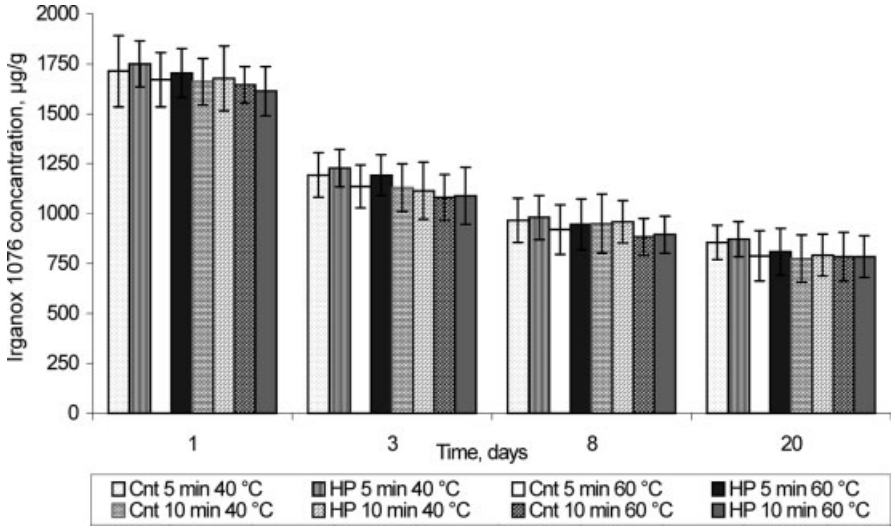

Figure 1. Concentration of Irganox remaining in the PP film (2.0 mg g^{-1} resin) in contact with the 95% ethanol solution, after HPP at 800 MPa.

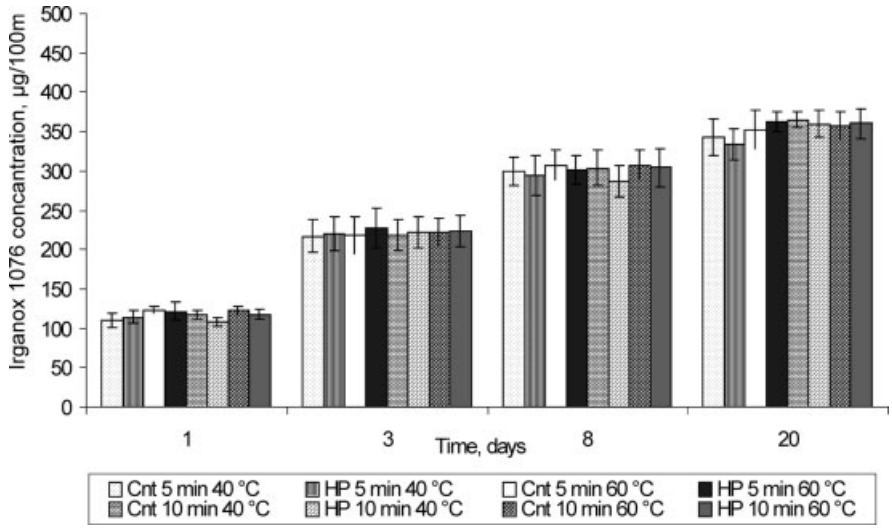

Figure 2. Concentration of Irganox in the FSL (95% ethanol) after contact with PP (2.0 mg g^{-1} resin) pouches HPP at 800 MPa.

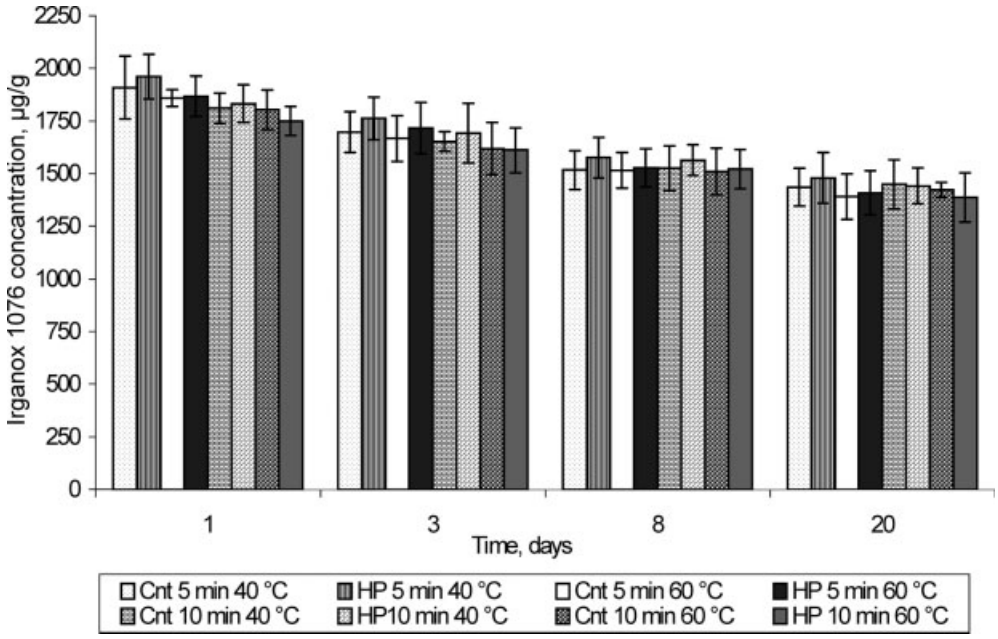

Figure 3. Concentration of Irganox remaining in the PP film (2.0 mg g^{-1} resin) in contact with 10% ethanol, HPP treated at 800 MPa.

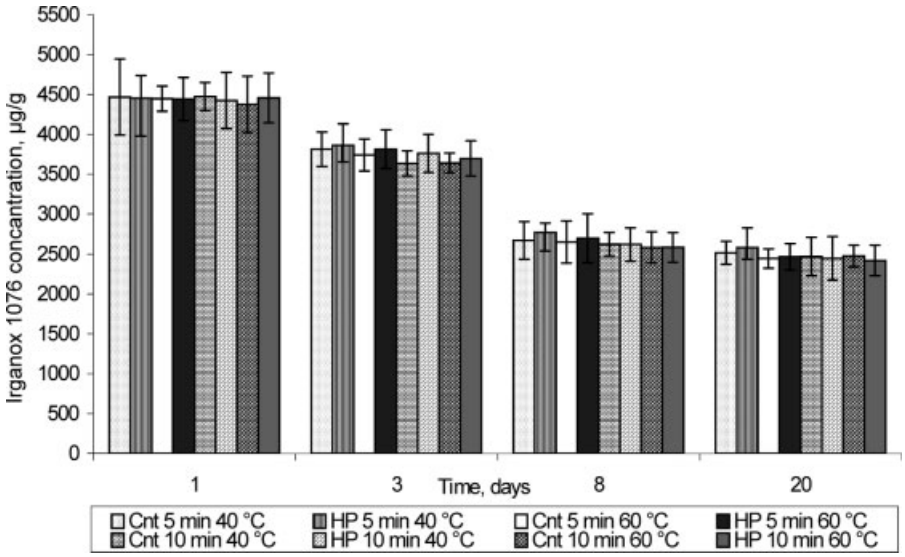

Figure 4. Concentration of Irganox remaining in the PP film (5.0 mg g^{-1}) in contact with the 95% ethanol solution HPP at 800 MPa.

After 1 day, the Irganox in the PP material in contact with 95% ethanol was in the range 882.5–980.2 µg g^{-1} polymer for the 2.0 mg g^{-1} PP, and 4473.0–4378.0 µg g^{-1} polymer for the 5.0 mg g^{-1} PP samples in both pressure-treated and control samples (Figs 1 and 4). After 20 days the PP–95% FSL system had values of 774.4–871.1 µg g^{-1} polymer for the 2.0 mg g^{-1} PP, and 2446.0–2581.0 µg g^{-1} polymer for the 5.0 mg g^{-1} PP samples for both treated and control (Figs 1 and 4) samples. After 1 day the amount of Irganox that migrated into 95% ethanol FSL was 110.20–123.5 µg 100 ml^{-1} for 2.0 mg g^{-1} PP and 241.8–253.8 µg 100 ml^{-1} for the 5.0 mg g^{-1} PP, both treated and control (Figs 2 and 5). After 20 days, the PP–95% FSL system had between 333.5 and 364.5 µg 100 ml^{-1} for the 2.0 mg g^{-1} PP (Fig 2), and between 807.6 and 838.3 µg 100 ml^{-1} for the 5.0 mg g^{-1} PP (Fig 5).

The migration of Irganox 1076 into 10% ethanol was very low (Fig 3) when compared with 95% ethanol (Fig 1). As shown in Figs 3 and 6, PP lost approximately 30% of its Irganox after one week of storage in contact with 10% ethanol. However, approximately 55% Irganox in the PP film was lost after one week of storage in contact with 95% ethanol FSL (Figs 1 and 4). The amount of Irganox remaining in the latter was very low after one week (Figs 1 and 4).

After 1 day the Irganox concentration in PP in contact with 10% ethanol was between 1511.2 and 1577.2 µg g^{-1} polymer, and after 20 days the respective values were 1388–1480.9 µg g^{-1} polymer (Fig 3). After 1 day the Irganox content in the PP film–10%

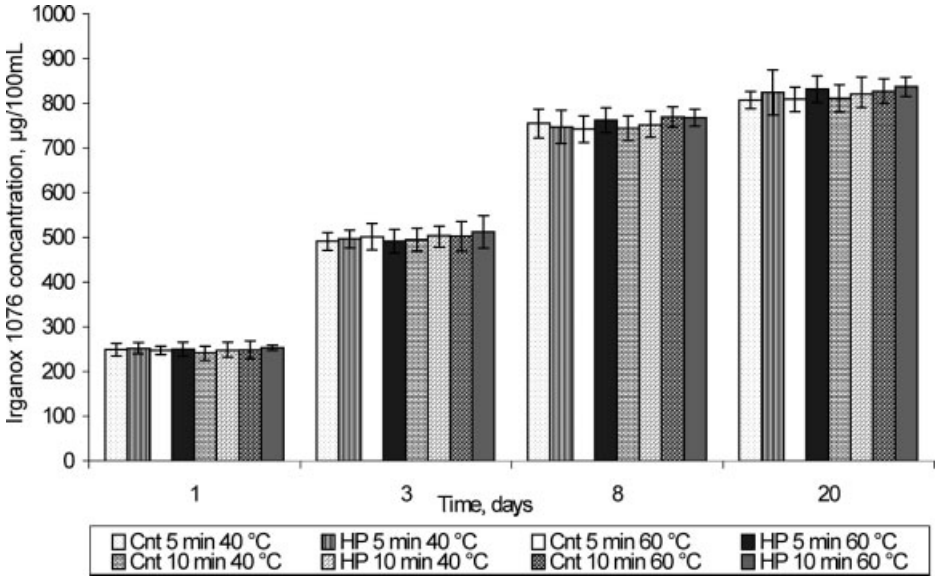

Figure 5. Concentration of Irganox in the FSL (95% ethanol) after contact with PP (5.0 mg g^{-1} resin) pouches HPP at 800 MPa.

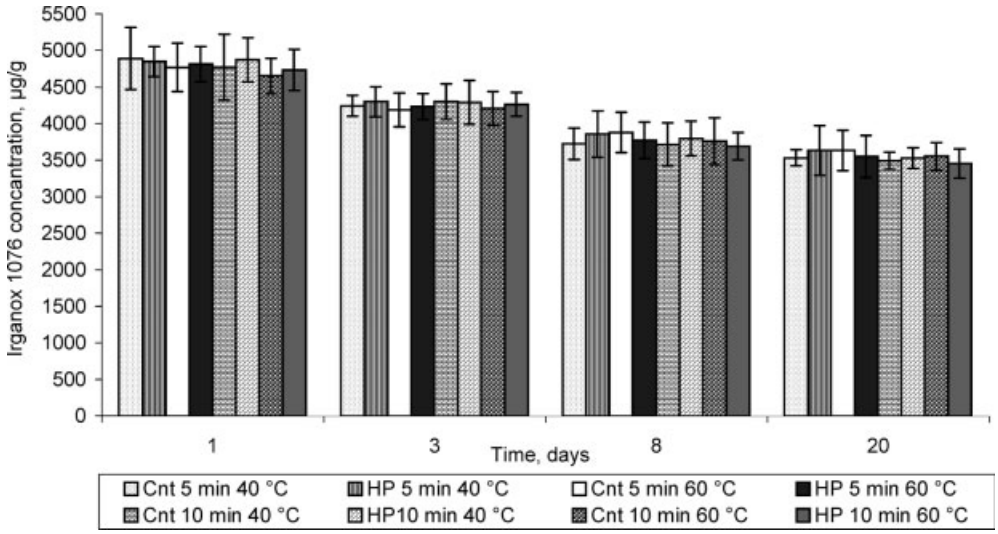

Figure 6. Concentration of Irganox in the PP (5.0 mg g^{-1}) film in contact with the 10% ethanol solution HPP at 800 MPa.

FSL system was 4893–4676 µg g^{-1} and after 20 days, the value was between 3531.0 and 3636.4 µg g^{-1} PP for the 5.0 mg g^{-1} PP system, both for HPP and control samples (Fig 6).

Migration of Irganox 1076 from PP to food-simulant liquids significantly increased and was dependent on the contact storage time. Migration through direct contact was dependent on the characteristics of the foodstuff, the contact time and antioxidant concentration in the PP. During storage, Irganox concentration in PP film significantly decreased, while the Irganox concentration significantly increased in the FSL (Figs 7 and 8).

In contact with liquids, plastics are subject to substantially increased migration depending on the chemical nature of the contact media. Liquid tends to penetrate plastic, causing dilation of the latter. Additives tend to distribute between two liquid phases, that which has penetrated the packaging material, and that in contact with the packaging surface. The migration of additives is thus clearly affected by the speed of penetration of the foodstuff into the packaging material. The effect of exposure time on Irganox 1076 migration into the two FSL, following HPP, was not significant. The HPP temperature had a significant effect on migration from the polymer and into the FSL. The Irganox concentration in PP film for 40 °C was 2578.9 µg g^{-1} polymer and for 60 °C was 2514.3 µg g^{-1} polymer. The Irganox concentration in the FSL was 1216.3 µg 100 ml^{-1} for 40 °C and 1285 µg 100 ml^{-1} at 60 °C. Temperature may influence mobility of the polymer chains and accelerate the diffusion of additives across the polymer structure.

In a detailed study on pouches made from: (1) PA–70 µm PE (medium density); (2) PA–60 µm PE (linear); (3) PA–40 µm PE; (4) PET–PVDC–PE; (5) PA–PE Surlyn; and (6) PA–PP–PE, the integrity of packages in contact with four simulants (distilled

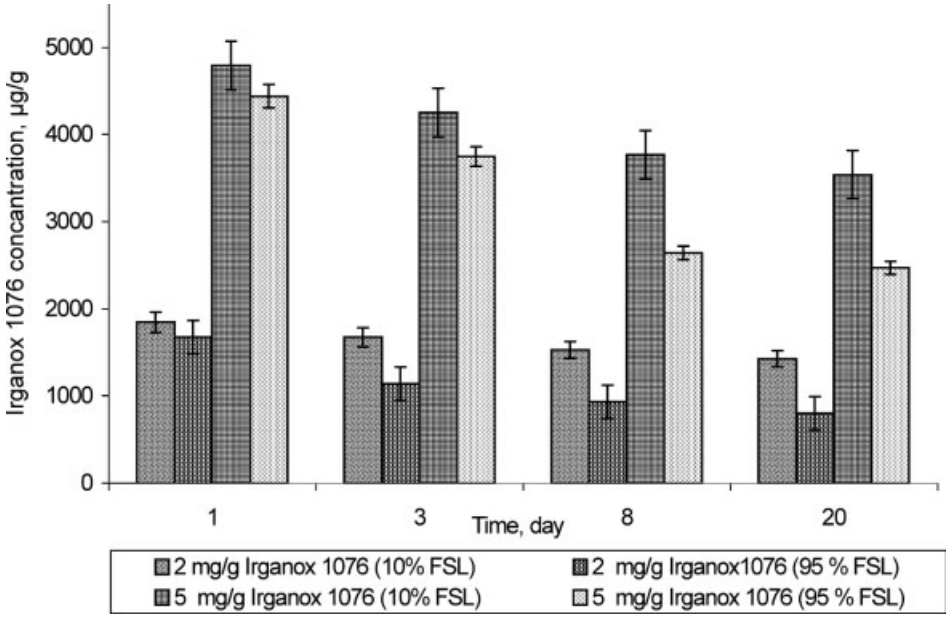

Figure 7. Influence of antioxidant level, time and food simulant on the LSMEANS of the Irganox 1076 remaining in the PP film.

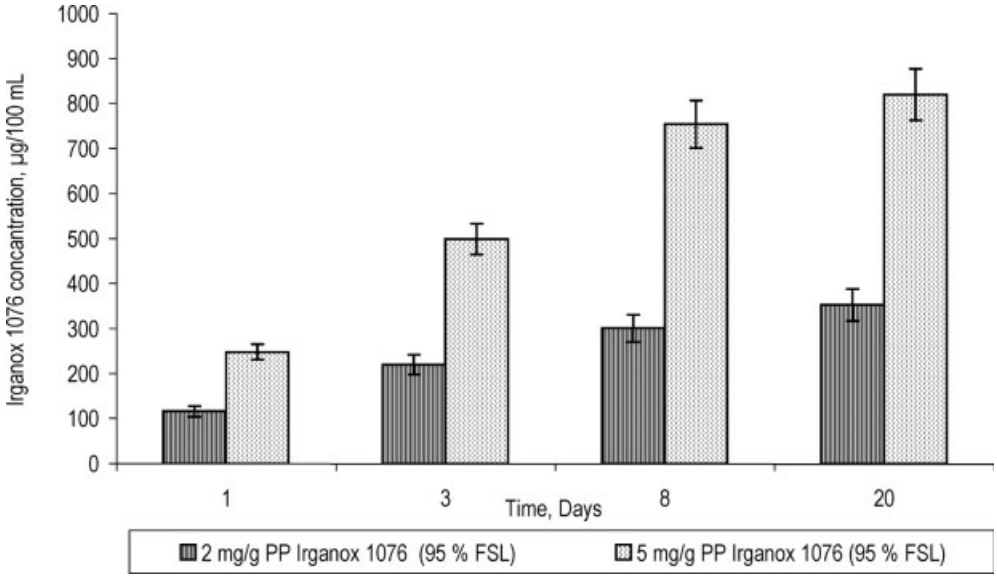

Figure 8. Influence of storage time and antioxidant level on the LSMEANS of the Irganox 1076 that migrated into the FSL.

water, 15% ethyl alcohol, 3% acetic acid, olive oil) for 10 days at 40 °C was evaluated by measuring global migration after HPP treatment (500 MPa for 30 min at 20 °C). There was no significant difference in global migration for pressure-treated and non-treated samples.[17]

The results of the present work are also in good agreement with those of Mertens,[18] who reported that HPP of five different films with four solvents (water, 4% acetic acid, 20% ethyl alcohol and *n*-heptane) at 25 and 60 °C had no effect on migration.

CONCLUSION

This research provides information on the migration of Irganox 1076 from PP into FSL after high-pressure treatment. Studies investigating additive migration from plastics into food simulants show that migration into foods is likely, especially if there is a long contact period. No significant differences in the migration level of Irganox 1076 from both materials were observed after HPP treatment into either FSL compared with the controls. Migration from PP film into 95% ethanol FSL was significantly higher than that into 10% ethanol FSL. Contact phase properties such as fat, alcohol content and acid content can influence migration behavior. Increasing the HPP temperature increased the migration of Irganox from PP to FSL. The migration of Irganox into the FSL significantly increased with storage time. Overall, these data indicate that migration from a single layer PP material did not significantly increase as a result of HPP.

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