Studies on the Volatile Compounds Generated on Irradiation of Flexible Films for Spice Packaging

M. Mizani\textsuperscript{1}, N. Sheikh\textsuperscript{2}, and M. Yousefi\textsuperscript{1}

ABSTRACT

Volatile compounds generated from two types of polymeric laminated films, irradiated by gamma radiation at 8, 10 and 15 kGy, were investigated. Activated carbon was used as a dry food simulant to trace the migrating compounds by Gas Chromatography/Mass Spectroscopy (GC/MS). The resulting data showed that the Polyethylene Terephthalate (PET)/Polyethylene Terephthalate (PET)/Linear Low Density Polyethylene (LLDPE) film was more resistant to gamma radiation as compared to Biaxial Oriented Polypropylene (BOPP)/Cast Polypropylene (CPP) film. Toxic radiolysis products migrated through both laminated films at 8 and 15 kGy gamma irradiation. The toxic products originating from additives formulated in adhesive and in direct food contact layers may be considered as high risk against the safety of dry foodstuffs such as spices.

Keywords: Dry food simulants, Gamma irradiation, Laminated films, Radiolysis products, Spice packaging.

INTRODUCTION

Spices constitute one of the main groups of dried food ingredients permitted to be decontaminated by irradiation treatment in numerous countries (EC, 1999; Farkas, 2001). The status of food irradiation in the world in 2005 was investigated and the main irradiated food products classified into five groups in which spices and dry vegetables were considered as the first group representing nearly half of the total irradiated substances (i.e., 46%) (Kume, 2009). In Iran, according to the survey of International Atomic Energy Agency (IAEA) and Legal Clearances of the International Consultative Group on Food Irradiation, several types of spices are allowed to be treated by gamma radiation in a process for up to 10 kGy (IAEA, 2003).

Although, decontamination of spices through irradiation is usually accomplished on prepackaged products to prevent their subsequent recontamination, it has been proved that irradiation may have some damaging effects on polymeric packaging materials which can lead to different structural changes by producing free radicals, ions and other low molecular weight radiolysis products (Komolprasert et al., 2008). Migration of these products into prepackaged-irradiated foodstuffs is highly probable that can affect their safety along with sensual characteristics (Galic et al., 2011; Arvanitoyannis and Tsarouhas, 2010; Morehouse, 2002; Sadler et al., 2001). Based upon toxicological aspects, many researchers have traced volatile compounds released from irradiated polymers diffusing into liquid food simulants (Makhzoumi, 1994; Goulas et al., 2004; Jeon et al., 2007).
Until 2002, dry foods containing no free fat, such as spices, used to be considered as safe and no food simulants were recommended (Ashby et al., 1997; Bradley et al., 2002; BSI, 2004; FDA, 2007). Despite that, in recent years researchers have been invited to study the possibility of migration, especially of volatile compounds, from multilayer packaging materials into these foodstuffs. A few research works have been published on the effect of irradiation on prepackaged dry foods, in which the products with no any food simulants have been put directly in contact with packaging material (Silva et al., 2008). Additionally, different dry food simulants are recommended for such migration tests as activated charcoal, Tenax, etc, each of which has been shown to have selective tendency for adsorption of migrated compounds (Schwope and Reid, 1988; Bradley et al., 2002).

The main objective of this research was to study the safety of two types of multilayer materials, namely Biaxially Oriented Polypropylene/Cast Polypropylene (BOPP/CPP) and Polyethylene Terephthalate/Polyethylene Terephthalate/Linear Low Density Polyethylene (PET/PET/LLDPE), which are commercially used for prepackaged irradiated spices in this country by determining the possibility of adsorption of migrating products released from these materials, on activated carbon as a dry food simulant.

**MATERIALS AND METHODS**

Two types of commercial flexible packaging materials, widely used for the case of spices, were selected: BOPP/CPP (total thickness: 50 µ, each layer: 25 µ) and PET/PET/LLDPE (thickness of individual layer 12/12/35 µ). Both the selected materials were laminated by polyurethane adhesive (two components and solvent free). These types of adhesives constitute one of the main groups used for lamination and are registered by FDA for food packaging (21CFR 175.105) (FDA, 2010; Svensson et al., 2001). Because of being free of solvent, these groups are safer with lower toxicity for dry foodstuffs packaged in multilayer polymeric films. Granular activated carbon was used as the dry food simulant (Sigma-Aldrich, 242268, 20-40 mesh particle size).

**Irradiation**

The multilayer films were irradiated by a 220 Gamma Cell (Atomic Energy of Canada, Ltd) at 8, 10 and 15 kGy. Co-60 was used as the gamma ray source. The average dose rate was 1.35 kGy h⁻¹. The radiation process was carried out in the presence of air at room temperature. This condition is commercially employed for irradiation of prepackaged spices (ASTM F1885-04, 2004).

**Migration Tests**

According to British Standard method for single surface testing, using a pouch, 100 g of activated carbon was placed into a pouch made from each type of multilayer films with 200 cm² of contact area (BSI, 2004). The prepared pouches were irradiated at the above given absorbed doses. Radiolysis compounds which may have migrated from packages were adsorbed onto the surface of the activated carbon and then collected by being dissolved into liquid carbon disulfide (CS₂, Merck, 102211). One gram of activated carbon was placed in 10 mL of CS₂ and extracted for 40 min in an ultrasonic bath. The desorbed solution was filtered through a sintered glass funnel and then 1µL of filtrate was analyzed through GC/MS (Lornage et al., 2005). Additionally released compounds from non-irradiated vs. irradiated activated carbon with no packaging were also analyzed under the same conditions (Figure 1).

GC/MS system consisted of a Thermoquest-Fining Trace Gas Chromatograph and a Mass Trace Mass Spectrometer. The gas chromatography operation was run under the following conditions: carrier gas: helium, oven temperature program: 60 to 250°C at a
rate 8 °C min⁻¹. Separation was carried out on a DB-1 silica capillary column (60 m×0.25 mm i.d.). Mass spectrometry was performed under the conditions of: electron energy of 70 eV and ion source temperature of 250°C. Volatile/or non-volatile compounds were identified by comparing the mass spectra of the recorded chromatographic peaks with those from the GC/MS system using NIST and Wiley libraries.

**RESULTS AND DISCUSSION**

Radiolysis products, identified after irradiation of both types of multilayer films at 8, 10 and 15 kGy, as determined by GC/MS are given in Table 1. These results only include the compounds identified with match factors greater than 85% and released from the irradiated films at different absorbed doses. The results of chromatograms of non-irradiated films as well as non-irradiated plus irradiated activated carbon (the peaks at RT: 6.47, 11.14, 11.72 and 19.27 minutes) are excluded from Table 1. The typical chromatograms of both types of multilayer films (control and treated at 15 kGy) as well as activated carbon (treated at 15 kGy) are shown in Figure 2.

Some of the released compounds, given in Table 1, such as 1, 2 benzene carboxylic acid which may be a degradation product of the phenolic UV stabilizers of polyolefins have been identified by many of the previous researchers (Chytiri et al., 2005). In the present research, migration and adsorption of this carboxylic acid on activated carbon is identified only in the chromatogram of the BOPP/CPP film, irradiated at 8 kGy, and not at higher doses. It seems that the level of this released compound is decreased through an increase in the radiation dose. This result is in agreement with the semi-quantitative analysis data reported by Chytiri et al. (2005) who observed a 50% lower concentration of carboxylic acid at 10 kGy.
Table 1. Radiolysis compounds released from irradiated BOPP/CPP and PET/PET/LLDPE film at different doses.

<table>
<thead>
<tr>
<th>Radiation doses (kGy)</th>
<th>Irradiated BOPP/CPP film</th>
<th>Irradiated PET/PET/LLDPE film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>RT (min)</td>
<td>Identified compounds c</td>
<td>RT (min) Identified compounds</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(min)</td>
</tr>
<tr>
<td>10.70</td>
<td>Cyclodecamethylpentasiloxane</td>
<td>13.72</td>
</tr>
<tr>
<td>13.73</td>
<td>2-Methyldecane</td>
<td>13.73</td>
</tr>
<tr>
<td>14.75</td>
<td>Cyclododecamethylhexasiloxane</td>
<td></td>
</tr>
<tr>
<td>17.62</td>
<td>No library match</td>
<td>19.45</td>
</tr>
<tr>
<td>17.84</td>
<td>No library match</td>
<td>23.68</td>
</tr>
<tr>
<td>20.67</td>
<td>1-Dodecanol</td>
<td>20.46</td>
</tr>
<tr>
<td>22.31</td>
<td>9,12-Octadecadienoic acid (z,z)-2,3-bis[(trimethylsilyl)oxy] propyl ester</td>
<td>25.11</td>
</tr>
<tr>
<td>22.73</td>
<td>1,2-Benzene dicarboxylic acid (0.45)</td>
<td>31.61</td>
</tr>
<tr>
<td>23.73</td>
<td>Heneicosane (0.12)</td>
<td>31.85</td>
</tr>
<tr>
<td>27.02</td>
<td>Tricosane (0.15)</td>
<td>31.93</td>
</tr>
<tr>
<td>32.70</td>
<td>Heptacosane (0.35)</td>
<td>32.50</td>
</tr>
</tbody>
</table>

\(^a\) The values in parenthesis represent relative areas; \(^b\) Retention Time, \(^c\) Match factor > 85%. \(^d\) Biaxial Oriented Polypropylene (BOPP)/Cast Polypropylene (CPP). \(^e\) Polyethylene Terephthalate (PET)/Polyethylene Terephthalate (PET)/Linear Low Density Polyethylene (LLDPE).
Figure 2. GC/MS spectra of non-irradiated and irradiated films plus irradiated activated carbon at 15 kGy: (a) Irradiated activated carbon; (b) Non-irradiated BOPP/CPP film; (c) Irradiated BOPP/CPP film; (d) Non-irradiated PET/PET/LLDPE film, and (e) Irradiated PET/PET/LLDPE film.
as compared with 5 kGy. However, 8 kGy is usually considered as a safe dose for irradiation of foodstuffs, including different types of spices (ASTM, 2004), but according to the results of this research, migration of carboxylic acids as volatile compounds is more likely to occur at lower doses of radiation (i.e., 8 kGy). Adsorption of these toxic and carcinogen benzene derivatives by such dry foodstuffs as spices may be possible and should be considered as a risk for consumers. 1-Dodecane and 2-methyl decane are linear hydrocarbons that are usually included in the list of radiolysis products of polyolefins (Makhzoumi, 1994; Buchalla et al., 1993). Additionally such volatile aromatic hydrocarbons, as naphthalene, have been isolated from non-irradiated and irradiated EVA and PET/PE/EVOH/PE films, kept at 80°C (Riganakos et al., 1999). Throughout this research such an aromatic compound as naphthalene is identified only in the chromatogram of BOPP/CPP film, irradiated at 15 kGy and at room temperature. Therefore, it may be concluded that irradiation at relatively higher absorbed doses may accelerate the migration of this aromatic compound even at lower temperatures. It has also been reported that these migrants could adversely affect the odor/flavor of foodstuffs (Riganakos, 1999; Welle et al., 2002) which is the most important specific property of spices. Additionally, some of the peaks are observed in either of the chromatograms (irradiated and non-irradiated samples) although the main point is that the peak areas for non-irradiated samples are probably too small to be detected, as the system didn’t give any signal as related to their presence.

Radiolysis products released from the second multilayer film (PET/PET/LLDPE) are given in Table1. These products include some such saturated hydrocarbons as, 2-methyldecane and penta-, hepta- as well as octadecane which have been previously reported as released volatile compounds from PET/PE/EVOH/PE multilayer film (Riganakos, 1999). A group of compounds (Table 1) which are rarely reported as radiolysis products of polymeric films include: heneicosane, tricosane, nonacosane, docosane and tetracosane, all commonly termed as “cosanes”, are non-polar and could be strongly adsorbed, especially on activated carbon surface (Bradley, 2002; Lago et al., 2003). Kim-Kang and Gilbert (1991) have extracted these hydrocarbons from non-irradiated and irradiated PET/PVDC/PE films by soxhlet method. They may be degradation products of some such plastic additives as anti-blocking agents, e.g., tetracosanamide and hexacosanamide, following irradiation (Kim-Kang, 1991; Hoening, 2006). Additionally these compounds may have been used in the formulation of polyurethane (PU) adhesives as a hydroxy carbonylic acid (such as hydroxyl docosanoic acid) to produce modified MDI prepolymer (Kroplinski, 1978; Randall, 2002). Therefore, it may be hypothesized that irradiation may cause some degradations in the adhesive layer of laminated films and the released compounds which diffuse out from the inner layer (i.e., CPP or LLDPE) are probably adsorbed on activated carbon. Kim-Kang and Gilbert (1991) have also reported the effect of irradiation on PU-adhesive layer of laminated films which might degrade some adhesive polymer chains leading to the release of potential migrants. Meanwhile, Chytiri et al. (2008) studied a type of multilayer film, comprised of recycled LDPE in the middle layer, showing a number of compounds detected in the food simulant possibly generated from the buried layer.

From the safety point of view, the cosanes are reported to be mild irritants especially to sensitive skins (Carlon, 1991). These straight chain alkanes may be considered as constituents of petroleum hydrocarbons. Based on toxicological investigations, the estimated Lowest Oral Adverse Effect Limit (LOAEL) for intermediate immunological/lymph reticular and for hepatic effects in animals are 250 mg kg⁻¹ day and 2000 mg kg⁻¹ day, respectively (ATSDR,1999).
CONCLUSIONS

Based on the results, activated carbon may be used as a dry food simulant for spices to trace the migrated compounds from the packaging material during gamma irradiation. Some toxic compounds may be released from the adhesive and as well from the inner layers of both types of irradiated laminated films. Therefore, regarding the safety aspects, none of the multilayer films may be suggested for irradiated prepackaged spices. Based on our previous research, the mechanical and barrier properties of PET/PET/LLDPE multilayer film have been less affected during irradiation as compared with BOPP/CPP (Mizani, 2009). Therefore, studies may be suggested to evaluate the suitability of rigid PET containers (in which adhesive and inner heat sealable layers would not be needed) for packaging of dry foodstuffs. This packaging material has been previously tested for medical devices irradiated at 25 kGy (Komolprasert et al., 2001). As for prepackaged foodstuffs, treated by irradiation at a lower dose of 10 kGy, especially under vacuum conditions, details may be taken into account in future studies.

ACKNOWLEDGEMENTS

The contribution by Mr. T. Ashtiani from Plastics Alvan Machine Co. Ltd for providing polymer films is hereby greatly appreciated.

REFERENCES

مطالعه ترکیبات فرار آزاد شده طی فرآیند پرتودهی فیلم های انعطاف پذیر بسته

م. میزانی, ن. شیخ, و م. یوسفی

در این تحقیق ترکیبات فرار آزاد شده از دو نوع فیلم پلیمری چند لایه که در سه ذخیره کیلوگرمی پرتو داده شده اند، بررسی شده است. به منظور رعایت ترکیبات مهاجرت کننده از کریین فعال بعنوان ماده مشابه غذایی بیای محصولات خشک در روش گاز کروماتوگرافی/ اسکیپتسر گرافی جرمی استفاده شد. نتایج نشان داد که فیلم پلی اتیلن ترفنلات/ پلی اتیلن سیبک خطي در مقابل پرتودهی گاما مقاومتر از فیلم پلی پروپیلن خطي شده در جهت دو محور / پلی پروپیلن ساده می باشد. ترکیبات سمی رادیولی از هر دو نوع فیلم در میزان کیلوگرمی آزاد شده و مهاجرت کرده است. ترکیبات سمی ناشی از تکسیونی های بکار رفته در لایه های جسب و در تمام با محصول

بعنوان خطر مهمی از نظر ابعادی محصولات غذایی خشک توجه ادمی ها محروم می شوند.